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Dense Nonaqueous Phase Liquids --

A Workshop Summary

Dallas, Texas
April 16-18, 1991

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Contents

1. Introduction 1

2. Summary and Conclusions 1

3. Background 2
   3.1 Extent of problem 2
   3.2 Types of DNAPLs 3
   3.3 Movement of DNAPL in the subsurface 3
   3.4 Identifying a DNAPL site 4
      3.4.1 Soil 4
      3.4.2 Ground Water 5

4. DNAPL Site Characterization 5
   4.1 Conceptual Approach 5
   4.2 Noninvasive Techniques 6
   4.3 Invasive Techniques 7

5. DNAPL Remediation 8
   5.1 Containment versus Restoration 10
   5.2 DNAPL Recovery Methods 10
   5.3 Enhanced DNAPL Recovery Methods 10
      5.3.1 Induced Gradient/Water Flooding 10
      5.3.2 Chemically Enhanced Recovery 11
      5.3.3 Thermally Enhanced Recovery 11
   5.4 Pump and Treat 11
   5.5 Vacuum Extraction 12
   5.6 Bioremediation 12
   5.7 Treatment Train 12

Table 1 14

Appendices

Appendix A: Dense Nonaqueous Phase Liquids, a USEPA Ground-Water Issue Paper 23
Appendix B: DNAPL Bibliography 47
Appendix C: DNAPL Workshop Attendee List 71
Appendix D: Glossary of Terms 77

1. Introduction

Dense nonaqueous phase liquids (DNAPLs) in the subsurface are long-term sources of ground-water contamination, and may persist for centuries before dissolving completely in adjacent ground water. In response to increasing recognition among scientists and engineers that DNAPL contamination is widespread, a two-day workshop concerning DNAPL site characterization and remediation was held in Dallas, Texas on April 16-18, 1991. The workshop was sponsored and organized by EPA's Ground Water Forum, Robert S. Kerr Environmental Research Laboratory, and Office of Solid Waste and Emergency Response, and the University of Waterloo, Ontario, Canada. Professionals from government, academia, and private industry with experience in DNAPL contamination presented papers and participated in discussions concerning the options for characterization and remediation of DNAPL sites.

This document was prepared to summarize the main observations and conclusions of the meeting, and draws freely from transcripts, papers, and comments prepared by the participants. A second meeting of the participants was held in Dallas on September 5-6, 1991 to review the draft summary. The summary is intended to be a nontechnical document of general interest to environmental scientists and engineers from Federal, State, and local agencies, universities, and private industry. Readers interested in more specific technical information should consult the extensive bibliography compiled in Appendix B. The material presented here represents "state-of-the-art" information, and, as such, can be expected to change as the science progresses.

To provide background material and an overview of the DNAPL issue, an EPA Ground Water Issue Paper entitled "Dense Nonaqueous Phase Liquids" (Huling and Weaver, 1991) is included as Appendix A. Appendix B is an extensive bibliography concerned with DNAPLs, and Appendix C is a list of workshop participants. Appendix D is a list of terms and definitions.

2. Summary and Conclusions

- The potential for extensive contamination of ground water by DNAPLs is high, but reliable, quantitative information concerning the extent of contamination is not currently available. Historically, many site investigations were not designed or equipped to detect or delineate the presence of DNAPL. As DNAPL awareness increases, an improvement in the quality of site characterization, and, therefore, DNAPL remediation, can be expected.

- Failure to directly observe DNAPL at a site does not mean it does not exist. Often, only very low aqueous concentrations of DNAPL constituents are detected in monitoring wells at known DNAPL sites. If dense, free-phase chemicals were widely used, handled, and disposed of according to standard industry practices common more than several years ago, chances are high that DNAPL is present. Indirect detection methods, based on soil and ground-water chemical compositions, can often be used to infer the presence of DNAPLs.

- DNAPLs can be broadly classified on the basis of physical properties such as density, viscosity, and solubility. Of the various types of DNAPLs found in the subsurface, chlorinated solvents and creosote/coal tar are apparently the most common. These two types of DNAPLs, however, present ground-water and remediation problems of a very different nature due to differences in their physical properties. Some of the conclusions applicable to one are not generally applicable to the other. Physical characteristics can guide the choice of characterization and remediation options.

- The relative importance of the forces that control the rate, flow direction and ultimate fate of DNAPL is different from the relative importance of those that control the distribution of dissolved-phase plumes. DNAPL behavior is only loosely coupled, if at all, to the behavior of water. Movement of DNAPLs is remarkably sensitive to the capillary properties of the subsurface, and the distribution of those properties controls the distribution of the DNAPL. Thus, knowledge of geologic conditions is relatively more important than knowledge of hydrologic conditions for adequate conceptualization and characterization of DNAPL sites.

- Obtaining a detailed delineation of subsurface DNAPL distribution is difficult and may be impractical using conventional site characterization techniques. DNAPL migrates preferentially through relatively permeable pathways (soil and rock fractures, root holes, sandy layers, etc.) and is influenced by small-scale heterogeneities (such as bedding dip and slight textural changes) due to density, capillary forces, and viscous forces. As a result, the movement and distribution of DNAPL is difficult to determine even at sites with relatively homogeneous soil and a known, uniform DNAPL source. This difficulty is compounded by fractured bedrock, heterogeneous strata, mixtures of DNAPLs, etc. The relative importance of small-scale heterogeneities may depend on the volume of the release.

- The risk of causing DNAPL remobilization must be assessed during site investigation. Conventional drilling technologies have a high potential for promoting vertical DNAPL movement. The appropriate investigation strategy is dependent on site-specific conditions, including the geology and the type of DNAPL. Nonintrusive, low-risk investigation methods such as surface geophysical techniques and reviews of site history and existing data should first be used to develop and improve the conceptual model of DNAPL presence and lessen the risks associated with subsequent drilling.

- Currently, surface geophysical methods capable of delineating subsurface DNAPL and the availability of geophysicists trained in investigating DNAPL problems are extremely limited. However, even routine, noninvasive geophysical techniques can be used to evaluate site geology, which has a great influence on DNAPL migration.

- Site characterization should be a continuous, iterative process, whereby each phase of investigation and remediation is used to refine the conceptual model of the site. The time required to define site characteristics cannot easily be reduced because of the heterogeneous, site-specific nature of subsurface environments and the evolutionary process required. However, the information required to implement early containment of dissolved-phase contamination is less extensive than that required to design final remedial alternatives.

- DNAPL in fractured rock poses exceptionally difficult problems for site investigation and remediation because fracture networks are complex, DNAPL retention capacity (mass of DNAPL per unit volume of rock) is generally small, and the depth to which DNAPL may penetrate can be very large.

- DNAPL, as a long-term source of dissolved phase ground-water contamination, is a pollution prevention issue. Unless controlled and/or remediated, DNAPLs in the subsurface may persist for decades or centuries dissolving into and contaminating vast quantities of ground water.

- Factors controlling DNAPL dissolution into ground water include the effective aqueous solubility of DNAPL chemicals, ground-water velocity, DNAPL-water contact area, and the diffusion of DNAPL chemicals in water.

- Ground-water remediation is a relatively new science. Rigorous scientific performance evaluations of existing remediation systems are essentially nonexistent. Only within the last half-decade has ground-water remediation been attempted on a significant scale. Technologies for DNAPL recovery are generally unproven under field-scale conditions. There are no methods or series of methods which have been demonstrated to completely remove DNAPL from the subsurface; however, several experimental DNAPL recovery and treatment technologies have undergone limited laboratory and pilot-scale field testing.

- There are no proven technologies to restore DNAPL zones in aquifers to drinking water standards. There are, however, technologies available to remove some portion of the DNAPL. Significant benefit, including reduced DNAPL mobility, can often be realized by use of such technologies. Technologies such as pump-and-treat can often be used to control dissolved-phase contamination.

- As with remediation, physical and/or hydraulic containment of DNAPLs has not been adequately demonstrated under a variety of field conditions, particularly with respect to vertical containment. Performance evaluations will be necessary to compare containment with other remediation options, and effective containment design may require as much site characterization information as effective remediation design.

- The complexity of the DNAPL problem dictates that site investigators have a sophisticated knowledge of DNAPL contaminant hydrogeology. Most decisions regarding site investigations and cleanup depend on site-specific conditions regarding the types and volumes of DNAPL and local hydrogeologic conditions. Formal environmental education is critical for future success in remediation. Progress in education and research in subsurface restoration has been slow, due to a paucity of funding mechanisms.

3. Background

3.1 Extent of problem

The potential for extensive contamination of ground water by dense nonaqueous phase chemicals is high because of their widespread production, transport, utilization, and disposal. There are many DNAPL contamination sites in North America, and dissolved constituents derived from DNAPLs are frequently detected in ground-water supplies. The most common DNAPLs are chlorinated solvents (e.g., trichloroethylene, tetrachloroethylene, and trichloroethane), creosote, and coal tar. DNAPL contamination is associated with a wide range of industries and operations, for example:

- wood treatment operations (creosote);
- manufactured gas plants (coal tar);
- transformer oil production, reprocessing, and disposal facilities (PCBs and chlorinated solvents);
- chemical industry facilities (chlorinated solvents, pesticides, herbicides, and other dense organic compounds);
- steel industry coking operations (coal tar);
- dry cleaners (chlorinated solvents);
- electronic instrument manufacturers (chlorinated solvents);
- machine shops (chlorinated solvents);
- print shops (chlorinated solvents);
- metal works (chlorinated solvents);
- waste disposal facilities (all types)

3.2 Types of DNAPLs

Although DNAPL compounds exhibit a continuum of physical properties such as density, viscosity, solubility, and sorptive properties, it is imperative to examine the characteristics of common DNAPLs. Many chlorinated solvents are characterized by relatively high density and low viscosity. However, creosote and coal tar compounds have relatively lower densities and higher viscosities than chlorinated solvents. The important physical differences between compounds in each group lead to distinctive problems with regard to characterization and remediation.

Many chlorinated solvents have relatively low viscosities and specific gravities significantly greater than that of water. Thus, the nonaqueous phase of these compounds may be relatively mobile in the subsurface and the movement may be strongly influenced by gravity. The aqueous (dissolved) phase may also be relatively mobile due to the sorption properties and significant solubilities of some constituents. Therefore, dissolved contamination may migrate relatively large distances at some sites.

Creosote and coal tars typically have specific gravities only slightly greater than water, and viscosities ten or twenty times greater than water. The nonaqueous phase is, therefore, less mobile in the subsurface, and its movement may be less gravity-dominated than nonaqueous chlorinated solvents. Aqueous-phase creosote and coal tar constituents (predominantly polyaromatic hydrocarbons (PAHs)) are generally much less mobile than aqueous-phase chlorinated solvents due to lower solubilities and concomitant stronger sorption onto aquifer materials.

The differentiation of DNAPLs into groups is a useful, though artificial, division of a continuum of density, viscosity, and solubility differences. The advantage to this classification is that it clearly delineates types of DNAPLs on the basis of physical and chemical characteristics. Differences in physical characteristics control mobility of both the nonaqueous and aqueous phases. In turn, mobility considerations will determine site characterization methods and remedial options. For example, optimal methods to characterize a chlorinated solvent site with a mobile, nonaqueous phase may differ significantly from methods used to characterize a site contaminated with less mobile, nonaqueous creosote or coal tar. However, it is important to note that many sites are polluted with complex mixtures of DNAPLs.

3.3 Movement of DNAPL in the subsurface

The infiltration of a nonaqueous liquid into the subsurface is controlled predominantly by gravity, viscous forces, and capillary forces, which are in turn controlled by the interactions of water, soil/aquifer material, and the nonaqueous liquid. Properties of the nonaqueous liquid which influence its mobility include density, viscosity, and interfacial tension with water. Properties of the soil which influence mobility of the nonaqueous liquid include soil heterogeneity, intrinsic permeability, mineralogy, pore size, pore geometry and macropores. DNAPL migration is also influenced greatly by structural and stratigraphic features.

When released into the subsurface, gravity causes a DNAPL to migrate downward through the vadose zone as a distinct liquid. Vertical migration is accompanied by some lateral spreading due to capillary forces and spatial heterogeneities. Residual liquid remains trapped by surface tension in pore space as the DNAPL drains through the soil. DNAPLs also dissolve into residual soil water and vaporize into soil gas.

When sufficient DNAPL reaches the vicinity of the water table to overcome the capillary (entry) pressure, DNAPL penetrates the saturated zone, and continues to migrate downward driven by gravity. Preferential flow occurs where DNAPL encounters relatively permeable layers and fractures. The ultimate location of DNAPL in the subsurface may be far from the DNAPL entry location. In addition to accumulating in DNAPL pools, residual DNAPL is trapped in pore spaces within the saturated zone. The dissolution of DNAPL constituents into passing ground water may result in the contamination of large volumes of ground water.

Gravity forces generally dominate DNAPL movement until the immiscible liquid reaches a permeability contrast, which may be very subtle. Capillary forces may inhibit penetration of the DNAPL into the less permeable zone. Often, DNAPL will move along bedding planes in the direction of the geologic dip, even in a direction opposite to ground-water flow. The actual direction of DNAPL movement will depend on the dip of the underlying strata, the capillary and viscous forces, and the density contrast.

The magnitude of capillary pressure resisting entry of DNAPL into a water-saturated, porous medium is inversely proportional to the size of pore openings. DNAPL, therefore,

migrates preferentially through relatively permeable pathways such as fractures, root holes, and sandy layers, and may be influenced by small-scale textural changes. Clayey aquitards which are relatively efficient at limiting vertical water movement may not prevent downward leakage of DNAPLs through minute fractures and root hairs. Chlorinated solvents can migrate through openings smaller than a human hair (i.e., < 20 microns). Thus, the normal concept of a confining layer commonly used in hydrogeology may be inappropriate at DNAPL sites.

The extent of contamination caused by a DNAPL is related to the volume of DNAPL released to the environment, the physical site characteristics, the length of time since release, and the physical properties of the DNAPL itself. Most sites, where large portions of aquifers contain clearly identifiable free-phase DNAPL, are creosote or coal tar sites. However, low viscosity, high density, chlorinated solvents with relatively high solubilities can cause widespread nonaqueous- and aqueous-phase contamination. The nonaqueous phase of these solvents is also more difficult to locate in the subsurface than creosote and coal tar.

3.4 Identifying a DNAPL site

An important problem which should be addressed early in the evaluation of potential DNAPL sites is the determination of whether or not DNAPL exists at the site. The importance of this identification cannot be overemphasized. The presence of DNAPL at a site should dictate the methods used for site characterization, investigation of the extent of contamination, and remediation. The current consensus is that a site has a high probability of being a DNAPL site if chemical usage was appreciable, and usage and disposal were consistent with industry practices common more than several years ago.

Some DNAPLs, such as creosote and coal tar, can be readily identified by visual inspection of soil and rock samples taken during field investigation. Likewise, immiscible-phase chlorinated solvents can sometimes be identified in ground-water samples. Visual identification may be difficult, however, where the DNAPL is colorless, present in low residual content, or heterogeneously distributed. The inability to directly verify the presence of a DNAPL should not be taken as evidence of its absence. In the case of chlorinated solvents and other dense, low viscosity DNAPLs, it is particularly important to assess the presence or absence of the nonaqueous phase without drilling directly through a nonaqueous pool or lens. It is possible to drill through a DNAPL zone without detecting the DNAPL, and the risk of remobilizing and spreading contamination during drilling is significant.

There are methods of indirectly assessing chemical and physical characteristics of both soil and ground water to evaluate the presence of DNAPL in the subsurface. They are based on equilibrium partitioning theory, and require determination of total chemical concentrations, soil moisture content, porosity, organic carbon content, approximate composition of the possible DNAPL, sorption parameters, and solubilities.

3.4.1 *Soil*

If no visible DNAPL is present, there are no direct methods available to confirm the presence of residual DNAPL in soil samples. Qualitatively, soil samples which exhibit concentrations in the percent range are indicative of DNAPL contamination. However, DNAPLs may also be present at low residual saturations in soil samples. Analytical results from these samples may exhibit much lower constituent concentrations.

It is sometimes possible to qualitatively assess the presence of DNAPL in such samples using equilibrium partitioning theory. If no DNAPL is present, there is a theoretical maximum mass of chemical which can be contained in a soil sample. The theoretical maximum total soil concentration is determined by the solubility of the chemical in water, the saturated soil gas concentration, and the sorptive capacity of the soil. If the nonaqueous liquid exists, the theoretical maximum total soil concentration would be exceeded, and the calculated pore water concentration would exceed the chemical solubility. The conclusion would be that DNAPL is present in the sample.

DNAPL can be a single chemical component, or a mixture of several or many components. For mixtures, the dissolved-phase concentrations in equilibrium with the mixture can be estimated such that the effective solubility of a compound is equal to the mole fraction of the compound multiplied by its pure-phase solubility. This relationship is strictly valid only for ideal liquid mixtures, but errors in the estimation of effective solubility for complex hydrocarbon mixtures should be less than a factor of two. A common problem at sites suspected of having mixed chlorinated solvent DNAPL in the aquifer is the lack of encounter of free-phase DNAPL in cores or monitoring wells. In such cases, the theoretical solubilities of the components cannot be estimated reliably due to the lack of DNAPL composition data.

Solubility data reported in the literature for coal tar and creosote constituents and PCBs is usually solid-phase solubility. However, when estimating effective solubility of these compounds in a DNAPL mixture, liquid-phase solubility, which is often many times higher than solid-phase solubility, should be used.

Methods for evaluating DNAPL presence in soil are most reliable when significant residual is present, pore water-soil partition coefficients can be determined, and effective solubilities can be calculated. Conclusions on the presence of

DNAPL are less reliable when sorption coefficients and effective solubilities must be estimated. However, such calculations are currently the only means of assessing the possible presence of DNAPL in soil and, as such, should be routinely performed when DNAPL contamination is suspected.

3.4.2 *Ground Water*

Laboratory experiments demonstrate that aqueous-phase chemical concentrations in contact with nonaqueous-phase liquids approach effective solubilities (saturation) rapidly. For low and moderate ground-water flow rates, it would be logical to expect saturated dissolved concentrations in ground water leaving the DNAPL zone. However, saturated aqueous concentrations are rarely observed in ground water. Relatively low aqueous concentrations in the field probably result from (1) the variable distribution of DNAPL as residuals, lenses, and pools; (2) aquifer dispersion; (3) nonuniform ground-water flow; (4) dilution in monitoring wells; and (5) failure to account for effective rather than pure-phase solubilities. Importantly, field observations of low aqueous concentrations do not support the absence of a DNAPL phase. This has been demonstrated at known DNAPL sites.

Unless a monitoring well is installed very close to the DNAPL zone and the well intake is short, saturated or near saturated levels of dissolved constituents will not be observed. Depending on the distribution of DNAPL, ground-water concentrations of 1% or less of effective solubility can be found even in the immediate proximity of the DNAPL. At some sites where permeability and ground-water velocity are exceptionally large, the contaminant concentrations found in monitoring wells are far below the 1% level in areas where DNAPL is known or expected to occur. Therefore, detection of such concentrations should be viewed as indirect evidence of DNAPL presence, and detection of very low aqueous concentrations should not be interpreted as absence of DNAPL.

4. DNAPL Site Characterization

4.1. Conceptual Approach

Many characterizations at potential DNAPL sites were not designed to assess the presence or extent of subsurface DNAPL contamination. Due to low solubilities, DNAPLs are expected to persist for decades or centuries before completely dissolving in ground water. As a result, DNAPL acts as a long-term source of dissolved-phase ground-water contamination, resulting in large plumes with chemical concentrations that may greatly exceed drinking water standards. For example, one gallon of trichloroethylene can contaminate approximately fifteen million gallons of ground water to a level of 100 micrograms per liter. At most DNAPL sites, the mass of contaminant in the immiscible phase greatly exceeds the contaminant mass dissolved in ground water. Based on the adverse environmental and health impacts of subsurface DNAPLs, characterization of the nature, extent, and severity of DNAPL contamination is necessary to determine site-specific remediation approaches.

Site characterization should be conducted in an evolutionary, phased approach. Characterization begins with a review of pertinent site history and available information from regional and local studies. This information is used to formulate an initial conceptual model of contaminant transport and fate at the site. Each characterization phase should be designed to test the conceptual model. The information acquired from each phase is used to refine the model. This iterative process should be continued throughout the remedial design and remedial action phases to provide better site characterization.

Mathematical modeling of contaminant transport and fate processes for dissolved contaminants is a useful site characterization tool. However, a limited number of multiphase flow models are currently available for modeling DNAPL transport. Fluid flow in a two-phase (water, NAPL) or three-phase (water, NAPL, gas) system is highly complex. Many variables affect DNAPL transport and fate and it is generally impractical to obtain the necessary field data to accurately model DNAPL movement in the subsurface. Accordingly, the utility of modeling DNAPL transport and fate at a site is presently very limited compared to other ground-water modeling applications.

Subsurface heterogeneity affects the migration pathway of DNAPLs. DNAPLs migrate faster through relatively permeable features and rates of flow are influenced by subtle, small-scale heterogeneities. Migration and distribution of DNAPL are sensitive to the capillary properties of subsurface materials and the volume of DNAPL released. As a result, the movement and distribution of DNAPL may be complex and difficult to determine in detail, especially for low viscosity contaminants. This difficulty is increased where there is fractured rock, heterogeneous strata, mixtures of DNAPLs, and multiple release locations.

Fractured rock settings pose exceptionally difficult problems in site characterization due to the complexity of fracture networks. DNAPL flow in fractured rock is especially difficult to trace due to the low retention capacity and the large depth to which DNAPL may penetrate even where fracture openings are small. Contaminant investigation in karstic settings is also extremely difficult. Efficient techniques for characterizing such sites are not currently available.

Many sites are underlain by clayey soil aquitards which contain secondary permeability pathways such as fractures

and root holes. These openings are particularly common at shallow depths and in stiff clays, but may extend to considerable depth and facilitate DNAPL migration to lower aquifers. It is prudent to assume the presence of interconnecting features capable of transmitting DNAPL through a hydrogeologic aquitard. Therefore, characterization of units beneath hydrogeologic aquitards may be warranted at many sites.

For these reasons, information regarding geologic conditions is important for adequate conceptualization and characterization at a DNAPL site. This implies that much work should be focused on characterizing the geological setting including lithologic and stratigraphic features. Manmade features (e.g., utility corridors) may play a significant role as preferential migration pathways for DNAPL transport and should also be characterized. Adequate site characterization is essential for design and evaluation of both remediation and containment systems. The level of detail and type of data required will be site-specific and dictated by the potential remedial technologies. In addition, less site characterization information will generally be required to implement early containment of dissolved-phase contamination than to design final remedial alternatives.

An important consideration in conducting investigations at DNAPL sites is the risk of expanding the zone of contamination by creating pathways for DNAPL migration as a result of drilling. Remobilization of DNAPL during site investigation can have one or more of the following negative impacts: (1) increase in ultimate risk to receptors; (2) increase in difficulty and cost of site remediation; and (3) misinterpretation of monitoring data, sometimes on the side of conclusions indicating higher site risk or remediation difficulty than is actually the case. It is important to prevent downward migration of mobile, perched DNAPL. Soil contaminated with residual DNAPL can also be carried to greater depths during drilling and is a source for cross-contamination of hydrogeologic units. Given the difficulty in predicting the presence and distribution of subsurface DNAPL, the risks involved with drilling generally increase with proximity to the disposal site or release location.

The degree of risk is related to the physical properties of the particular DNAPL present. DNAPLs with relatively high densities and low viscosities (e.g., chlorinated solvents) are more mobile and more easily mobilized to greater depths than those with lower densities and higher viscosities (e.g., creosote and coal tar). Unlike creosote or coal tar contamination, which may be identifiable in subsurface material, many DNAPL chemicals (e.g., chlorinated solvents) may not be obvious during drilling. It is possible to drill through zones of DNAPL contamination without realizing it. Even when the locations of DNAPLs and the geology at the site are relatively well known, the installation of wells in DNAPL areas using the best available technology has its risks. For example, bentonite pellets used to form annular seals during well installation do not swell in the presence of certain DNAPLs. Consequently, an effective annular seal may not be achieved.

The risks involved in the use of invasive methods mandate evaluation of site history and existing data and using noninvasive techniques (e.g., surface geophysical methods), where applicable, prior to invasive studies (e.g., drilling of boreholes). The information derived from these sources can be used to formulate and refine the conceptual model for transport of DNAPL at a site and to guide the use of invasive techniques.

Methods used for determining DNAPL presence have generally been limited to analysis of soil samples, observations during drilling and other field activities, and DNAPL detection in wells. Assessment of DNAPL mobility has generally been limited to observing free-phase liquid in wells or seeps. There is a need to develop, demonstrate, and document (1) drilling methods which can be used to prevent or reduce the risk of downward DNAPL migration, including techniques allowing DNAPL detection while drilling; (2) improved field methods for rapid and inexpensive detection of DNAPL that cannot be readily identified by visual inspection of drilling samples; and (3) methods to evaluate DNAPL mobility.

4.2 Noninvasive Techniques

Noninvasive techniques which may be applicable to initial site characterization at DNAPL sites include soil gas analysis and surface geophysical methods. At certain sites, these techniques may provide useful site characterization information. Geophysical techniques have been applied with some success to characterization of site hydrogeology. However, geophysical techniques for detecting organic contamination have not been adequately tested in a variety of field situations. The methods discussed below, which have recently been applied to the detection of organic contamination, are relatively untested and should be considered as emerging technologies. These techniques are currently research tools and are not readily available or applicable for use at most sites. In addition, the use of noninvasive techniques generally would not eliminate the need for invasive characterization at a site. Instead, the results from noninvasive studies may provide information to guide the use of invasive methods.

Depending on site conditions, soil gas analysis may be useful in situations where volatile constituents are present. High vapor concentrations may be present near volatile, immiscible-phase contaminants in the unsaturated zone. Soil gas samples from areas where volatile constituents are not present in the immiscible phase or from areas where the immiscible phase is only present in the saturated zone may exhibit relatively lower or nondetectable constituent concentrations. The extent of

DNAPL contamination in the unsaturated zone may be relatively limited. Therefore, soil gas data should be examined for both trends and isolated high concentrations. These data may provide an indirect indication of immiscible-phase contaminants in the unsaturated zone.

Surface geophysical methods, where applicable, allow noninvasive investigation of subsurface physical and chemical properties. Variations of many of these methods are also useful borehole techniques. Seismic, electrical, magnetic, and ground penetrating radar techniques have been successfully applied in site characterization. These methods may provide valuable information such as depth to ground water and bedrock, lithologic and stratigraphic boundaries, fracture orientation, locations of buried pipes, trenches, and drums, and inorganic contaminant distribution, without risk of spreading contamination.

Ground penetrating radar, complex resistivity, and electromagnetic induction methods have been applied successfully to the detection of aqueous and nonaqueous-phase hydrocarbons and other organic chemicals at a very limited number of sites. Applications of these methods to organic contamination investigations are relatively untested and are state-of-the-art research techniques. Consequently, these methods are not currently available for use at most sites.

Ground penetrating radar is used to detect changes in dielectric properties of subsurface materials. These changes may be related to changes in physical properties such as water content or bulk density. Although principally used to aid in the characterization of stratigraphy and lithologic heterogeneity, this method has been used to map LNAPL.

Complex resistivity measures resistivity in magnitude and phase as a function of frequency. The method is used to detect the presence or absence of chemical reactions. Higher phase shifts and nonlinearity generally indicate greater chemical activity. The activity includes many clay-organic chemical reactions. The specific reactions which are occurring have not been characterized at most sites. However, the geophysical signatures from these reactions have been used to determine the presence of organic contamination. Recent laboratory investigations indicate most common organic contaminants react with montmorillonite and, therefore, may be detectable using this technique.

Electromagnetic induction methods, which are used to map changes in electrical conductivity in the subsurface, have been applied to the detection of organic chemicals with limited success. The conductivity of subsurface materials is predominantly a function of porosity, water saturation, electrical conductivity of the pore fluid, and the clay content of the soil. Dissolved inorganic contaminants generally increase the conductivity of the water and may mask any conductivity decreases due to the presence of organic chemicals. Electromagnetic induction methods are generally most applicable to organic contamination delineation when inorganic contaminants are not present or when immiscible-phase organic compounds preferentially wet soil, displace water, and decrease conductivity.

The value of geophysical methods may be increased when applied repeatedly at successive points in time. Changes in the geophysical signatures of subsurface materials may be indicative of contaminant migration. Geophysical methods are best suited to detect DNAPL while the immiscible liquids are moving. Repeated geophysical surveys may provide information concerning subsurface changes caused by the moving DNAPLs as well as identify the pathways along which they are moving. During remediation, repeated surveys may also be useful in monitoring changes caused by the remediation process.

The utility of geophysics at most sites will not be in the direct detection of DNAPLs, but in aiding the characterization of where DNAPLs may be going based on the geologic context. The use of geophysical methods to provide information concerning the hydrogeology at a site is within the current state of practice. The applicability of these techniques depends on site-specific conditions. All techniques are not appropriate for every site and applications must be evaluated on a site-specific basis.

Detection of organic compounds using geophysical methods is currently state-of-the-science and not readily available for use at most sites. The techniques have only been applied successfully at a limited number of sites and should be considered as emerging technologies. The principal difficulties related to the use of geophysical methods in characterizing organic contamination are partly due to deficiencies in the knowledge of contaminant properties and processes, but predominantly due to a critical lack of environmental geophysicists trained in these techniques.

4.3 Invasive Techniques

Regardless of the use of noninvasive characterization techniques, invasive methods will continue to be indispensable for characterizing most DNAPL sites. Invasive techniques include subsurface soil sampling, piezometer and monitoring well installation, and the use of such tools as standard or modified cone penetrometers. Soil, rock, and fluid samples brought to the surface should be carefully inspected and analyzed as drilling progresses to identify DNAPL pools, residual zones, and potential barrier layers. In addition, the type and degree of site characterization needed for application of one DNAPL remedial technology are often not what is best suited for another. Therefore, site characterization strategies appropriate for DNAPL sites are generally more complex than those that are adequate for non-DNAPL sites.

Two basic approaches to invasive characterization exist and have been referred to as the outside-in and the inside-out approaches. The outside-in strategy of conducting initial invasive characterization outside suspected DNAPL areas and working toward the source has the advantage of allowing acquisition of significant geologic and hydrogeologic data at relatively low risk. These data can be used to refine the conceptual model and guide additional investigations. However, it should be noted that uncertainty exists in determining the extent of the suspected DNAPL area at any site. One disadvantage to the outside-in approach is that much additional time and expense may be incurred during the study if characterization is started too far from the suspected DNAPL zone. At some sites, it may be appropriate to avoid drilling directly within areas of known or suspected DNAPL contamination and focus on characterizing dissolved contaminant plumes migrating from the source areas. However, drilling in suspected DNAPL areas may be required to provide the necessary information for site characterization and remedial design (e.g., assessing the presence and locations of DNAPLs and for application of in situ restoration technologies).

The inside-out approach of initially drilling within the areas suspected to be the most contaminated and subsequently drilling in more remote areas to define the extent of contamination has been the traditional approach for many site investigations. One potential advantage of this method is that fewer boreholes may be required to determine the extent of contamination when investigation is started within an area of known contamination and progresses outward. The obvious disadvantage to this strategy is the increased potential for providing pathways for the rapid downward migration of DNAPLs. The increased risks of remobilizing certain high mobility DNAPLs (e.g., chlorinated solvents) may render the inside-out approach the least desirable strategy at certain sites. This strategy appears to be most applicable at DNAPL sites where the immiscible liquids are relatively immobile (e.g., many creosote and coal tar sites). The relative time and cost advantages of the inside-out approach may be offset by additional investigation and remediation costs incurred if DNAPLs are mobilized to greater depths.

The choice of characterization strategy depends on the conceptual model of the site and the physical properties of the contaminants. Immiscible liquids with relatively high densities and low viscosities (e.g., chlorinated solvents) will be relatively more mobile than less dense, more viscous liquids (e.g., creosote or coal tar). More mobile liquids represent greater risk for spreading contamination to deeper zones during site characterization. In addition, these contaminants may have migrated considerably farther from the DNAPL entry location than less dense, more viscous liquids. The use of site history and noninvasive techniques may provide useful information for guiding invasive study. However, it will generally not be possible to determine the extent of immiscible liquids prior to invasive study. Locations for invasive study must be chosen using the best available site specific information and knowledge of DNAPL contaminant transport principles. Regardless of whether the outside-in or inside-out approach is chosen, characterization should proceed from shallow depths to greater depths. In this manner, more information is acquired concerning shallow geologic features and contamination and the risk of mobilizing DNAPLs to greater depths during drilling is reduced.

5. DNAPL Remediation

Experimental technologies must undergo considerable development in order to become proven technologies (Figure 1). During the experimental phase, problems and concepts are identified and numerous technologies are screened using bench study results. Technologies which pass the initial screening may be evaluated during controlled field studies with rigorous mass balance constraints. The most promising emerging technologies can then be further assessed during uncontrolled pilot investigations. Those technologies which produce favorable results may be implemented on a large scale. The time necessary for an experimental ground-water remedial technology to be considered proven varies, but may be on the order of ten years. The ultimate goal of a proven technology is to restore a contaminated aquifer in a cost-effective manner.

No in situ technologies for restoring DNAPL zones in aquifers to drinking water standards have been adequately demonstrated or subjected to rigorous scientific evaluation. Some technologies appear to hold promise for use in DNAPL remediation. The most promising technologies are considered emerging technologies. It is not possible at this time to fully evaluate the efficacy of the emerging or experimental technologies on the horizon due to the critical lack of data from controlled field studies. Table 1 provides a summary of remedial options potentially applicable at DNAPL sites.

Conceptually, a DNAPL site may be considered to consist of two contamination zones (Figure 2), the DNAPL zone which contains free-phase and/or residual DNAPL and the zone of dissolved (and sorbed) contamination only. The zone of dissolved contamination is formed by dissolution of DNAPL constituents into passing ground water and encompasses the DNAPL zone. The nature of contamination in each zone is different and, accordingly, potential remediation technologies for each zone also differ.

Technologies for containment and, potentially, restoration of contaminated ground water within areas contaminated solely with dissolved and sorbed constitutents are better defined than technologies for containment and/or restoration of DNAPL zones. However, effective implementation of technologies designed for restoration of the zone of dissolved

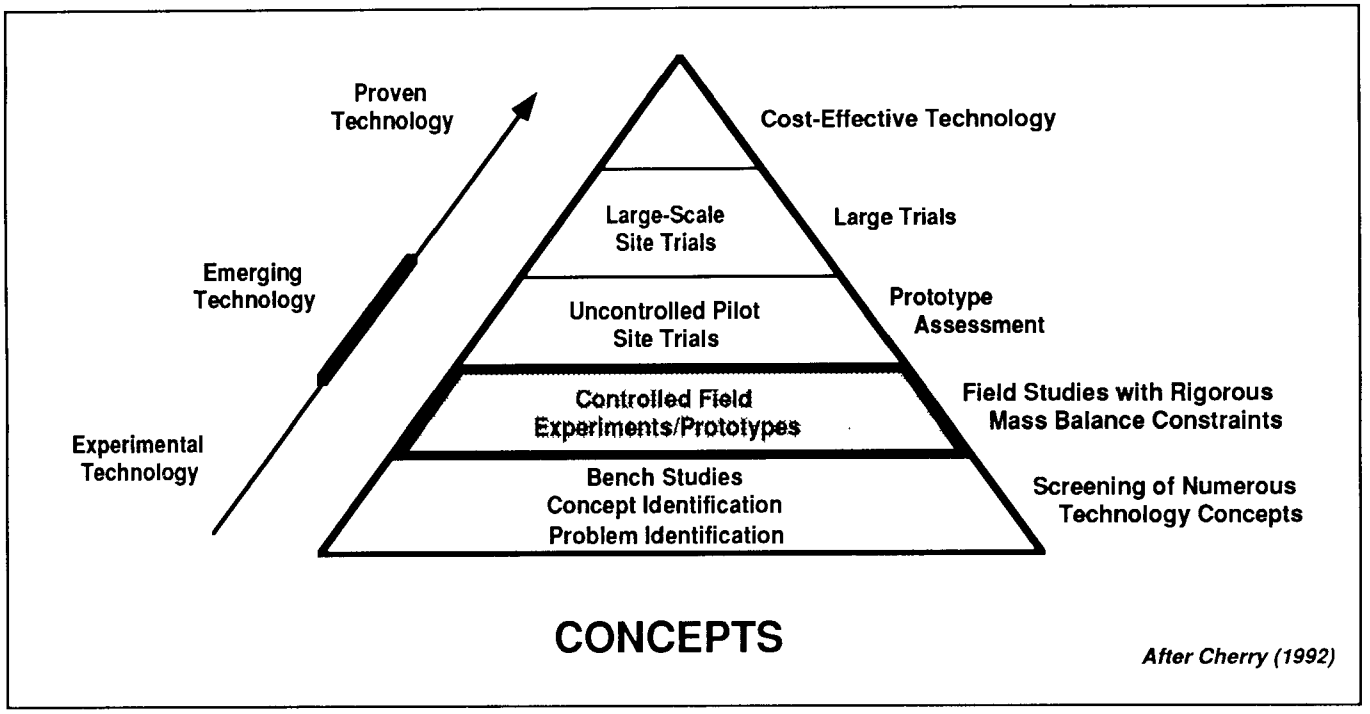

Figure 1. Conceptual Development of Technologies.

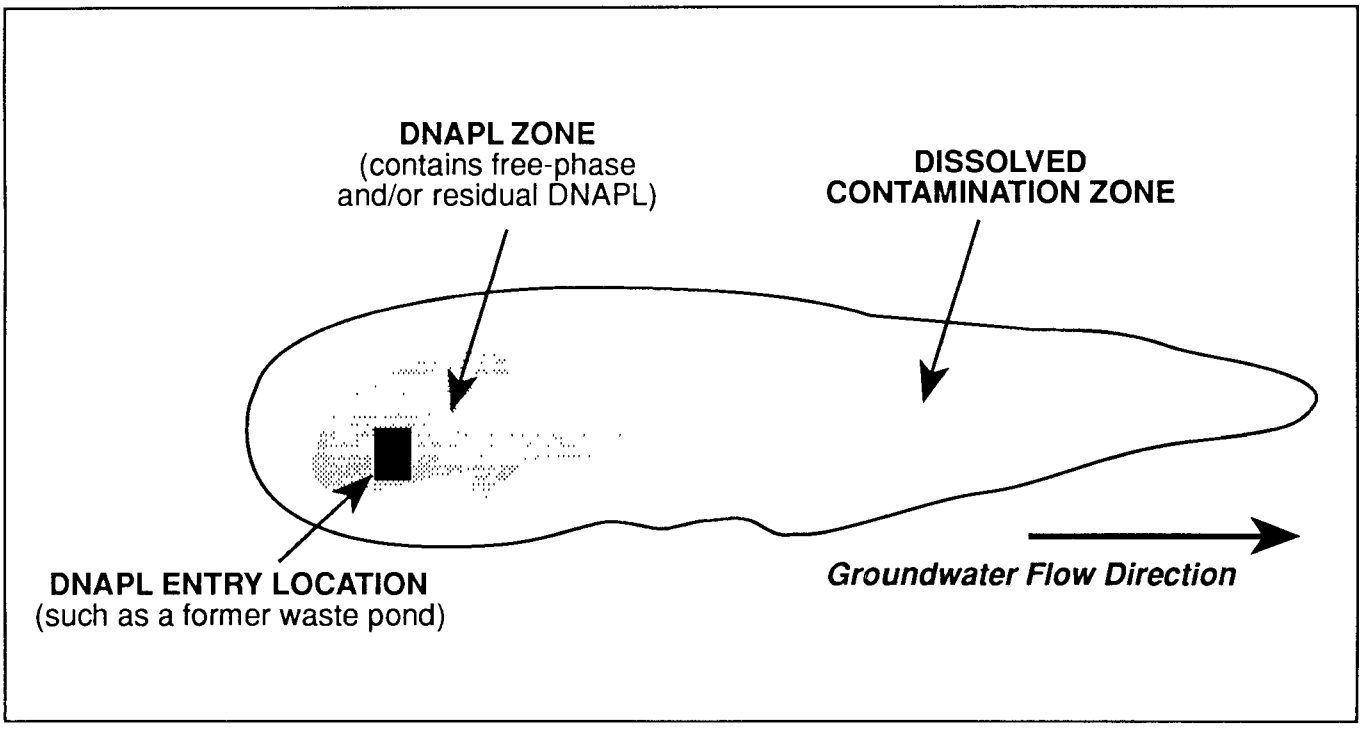

Figure 2. Defined Areas at a DNAPL Site.

contamination will require containment of ground water and DNAPL within the DNAPL zone. Technologies for DNAPL containment are promising but are not yet proven in a variety of field situations.

5.1 Containment versus Restoration

There is considerable scientific and political controversy concerning ultimate attainable cleanup levels at a DNAPL site. Except for excavation, there are no proven technologies to reduce the total mass of subsurface DNAPL to levels low enough to effect full restoration of a contaminated aquifer. However, there are techniques which can mitigate contamination at many DNAPL sites. Therefore, much attention in political, scientific, and industrial communities has focussed on the concept of "containment" versus "restoration." In this context, restoration refers to full and complete rehabilitation of the contaminated subsurface. Containment refers to physical control of the aqueous and nonaqueous phases in the subsurface and is commonly coupled with partial cleanup of dissolved contamination outside of the DNAPL zone. The hydraulic containment of dissolved-phase contamination is fairly well understood and technically feasible.

Although it is popular to envision containment of a nonaqueous phase by physical or hydraulic barriers such as cut-off walls, drains, wells, and artificial hydraulic gradients, these mechanisms have not been critically evaluated under a variety of field conditions, particularly for vertical containment. In addition, containment technologies require maintenance and monitoring following installation to ensure DNAPL isolation.

Horizontal and vertical containment of DNAPLs present different problems. Some scientific opinion holds that vertical migration of DNAPLs through low permeability strata can be limited or eliminated by creating an upward hydraulic gradient. However, these results are from modeling studies, and have not been demonstrated in the field. Natural conduits through aquitards and chemical-induced desiccation of the clays may allow downward vertical migration against a hydraulic gradient.

The physical and chemical properties of a DNAPL may influence the feasibility of containment and restoration options. For example, the containment of low viscosity, high density chlorinated solvents may not be possible under certain conditions due to their high potential for mobility. In contrast, highly viscous wastes (e.g., typical creosote and coal tar) may be more readily contained.

Physical containment cannot be effected unless the location of the potentially mobile DNAPL is known. To date, there are no adequate means of locating chlorinated solvent DNAPLs in the subsurface. Without adequate DNAPL zone delineation, containment may not be possible to attain or adequately demonstrate. Development of methods for site characterization is as critical for DNAPL containment options as it is for other remedial options.

5.2 DNAPL Recovery Methods

DNAPL recovery systems consisting of extraction wells or drain systems may remove large volumes of mobile DNAPL by extracting total fluids (DNAPL and water) or DNAPL only. The wells or drains are usually installed in stratigraphic traps to optimize recovery where DNAPL pools are present. The efficiency of a DNAPL recovery system generally decreases rapidly as the DNAPL saturated thickness decreases. Overpumping a product recovery well may result in truncation of the DNAPL layer and significantly reduce the formation transmissivity to DNAPL flow.

A significant quantity of DNAPL will remain trapped within pore spaces subsequent to the removal of mobile DNAPL. Generally, it will not be possible to reduce the DNAPL residual saturation by increasing the hydraulic gradients alone. This may be favorable in the sense that DNAPL is no longer potentially mobile under normal hydraulic gradients, and the high surface areas associated with residual ganglia and blobs allow greater dissolution per volume of DNAPL than with pools or lenses.

5.3 Enhanced DNAPL Recovery Methods

DNAPL recovery may be enhanced by injecting fluids or agents into the DNAPL zone to increase hydraulic gradients, reduce water/DNAPL interfacial tension, reduce DNAPL viscosity, and/or increase DNAPL solubility. However, there are practical technical problems which limit the effectiveness of these methods in the field. The complex subsurface distribution of DNAPL is a function of geologic heterogeneities. These heterogeneities, in conjunction with permeability reductions caused by the presence of DNAPL, can prevent injected fluids or agents from making thorough contact with subsurface DNAPL. The use of enhanced DNAPL recovery techniques in the area of hazardous waste remediation is in its infancy. Most of the techniques were developed for enhanced oil recovery (EOR) applications. Consequently, very little information is available concerning field applications of enhanced DNAPL recovery techniques.

5.3.1 *Induced Gradient/Water Flooding*

Where DNAPL is pooled on lower permeability layers, inducing DNAPL to flow to wells or drains may be an effective means of achieving significant mass removal. The feasibility of removing DNAPL through induced flow is influenced by site-specific characteristics such as pool thickness, DNAPL viscosity, hydraulic conductivity, relative

permeabilities, and capillary pressure-fluid content relationships.

Long-term DNAPL recovery is increased by maintaining a maximum thickness of DNAPL adjacent to the well or drain. Capillary pressure and DNAPL saturation increase with depth in a DNAPL pool, resulting in an increase in relative permeability of the media to DNAPL with depth. For this reason, DNAPL at the base of a pool is more mobile than DNAPL at the top of a pool. As the thickness of a DNAPL pool is reduced by pumping, the average relative permeability to DNAPL declines, resulting in greater resistance to DNAPL flow. This has important implications for the efficacy of induced gradient DNAPL removal systems.

Pumping water from wells or drains completed above a DNAPL pool causes DNAPL upwelling which results in an increase in formation transmissivity to DNAPL. Pumping wells or drains completed in the pool further induce DNAPL flow. To maximize the driving force on the DNAPL, drawdown on both the DNAPL pool and the water table should be maximized. This may be achieved with dual drain systems, dual well systems, an open trench to the ground surface, fully screened wells, or water injection wells. The physical and chemical properties (e.g., viscosity, interfacial tension, etc.) of a DNAPL will control its mobility and the extent to which the mobile product may be removed. Highly viscous wastes may be more difficult to mobilize, even under enhanced hydraulic gradients.

5.3.2 *Chemically Enhanced Recovery*

Surfactants, cosolvents, and alkaline agents are primarily used to increase the solubility of DNAPL constituents in ground water. The enhanced solubility increases the efficiency of contaminant removal by significantly increasing contaminant concentrations in ground water recovered by extraction systems. Surfactants are capable of increasing the solubility of many DNAPLs by several orders of magnitude.

However, in addition to increasing DNAPL solubility, surfactants enhance DNAPL mobility by lowering the interfacial tension between the nonaqueous phase and water. The reduction of interfacial tension can produce uncontrolled vertical and lateral migration of previously immobile DNAPL trapped as isolated ganglia, lenses or pools accumulated on lower permeability strata in the aquifer. The mobilization of such DNAPLs could greatly exacerbate ground-water problems at DNAPL sites.

Surfactants and polymers have been used by the petroleum industry to mobilize and recover a portion of the residual hydrocarbons from reservoirs. Polymers have been used to increase the viscosity of injected fluids and aid in the displacement of residual hydrocarbons. Recent laboratory studies have demonstrated that under the proper conditions, surfactants can enhance the removal of significant quantities of DNAPL. Although it is known that surfactants can enhance the rate of DNAPL mass removal, it is also known that complexities related to geologic heterogeneity cause limitations in mass removal such that restoration to drinking water conditions is currently problematic. Currently, several pilot studies are under way to evaluate the effect of surfactants on the solubility and mobility of DNAPL under field conditions.

5.3.3 *Thermally Enhanced Recovery*

The application of heat to viscous DNAPLs will enhance their mobility by decreasing viscosity and density. Additionally, heating DNAPL increases the solubility of some constituents. Steam and hot water flooding may be applicable in the unsaturated and saturated zones. The injected steam yields heat to the formation and condenses into a zone that acts as a hot water flood. Volatile DNAPL may condense to form a DNAPL front, resulting in increased DNAPL saturation and mobility. The continuous injection of steam drives the hot water and nonaqueous phase toward extraction wells. Heating certain DNAPLs may reduce their density, convert them to lighter-than-water NAPLs, and, thereby, promote mobility due to buoyancy forces and viscosity reduction.

Various steam and hot water displacement methods for DNAPL recovery have been evaluated in laboratory and pilot field studies. These methods have been successful at removing significant quantities of DNAPL from the vadose zone. However, the amount of residual DNAPL left in place will maintain contaminant levels above regulatory levels for a significant time.

5.4 Pump-and-Treat

Traditional pump-and-treat systems, which recover and treat aqueous contamination, may be useful components in many remediation programs. These systems may be used to prevent plume migration and reduce contaminant concentrations in areas contaminated solely with aqueous and sorbed constituents. Pump-and-treat may also be used to remove residual DNAPL by solubilization. However, these systems are not efficient at removing DNAPL from the subsurface. Many pore volumes of water are needed to completely remove even residual DNAPL under the best of circumstances. In general, subsurface heterogeneities limit the ability to move water through many contaminated zones, and thereby limit the ability of a pump-and-treat system to cleanse a site. However, when used in conjunction with other remediation techniques designed to remove DNAPL, pump-and-treat systems may prevent the exacerbation of ground-water problems by capturing and removing aqueous-phase contaminants.

5.5. Vacuum Extraction

Under certain conditions, soil vacuum extraction (SVE) technology has been demonstrated to remove large quantities of volatile DNAPLs from the vadose zone. This technique requires the application of vacuum to the unsaturated zone, thereby inducing air flow and enhancing the removal of many volatile organic contaminants (VOCs). The VOCs are removed from the subsurface by gas transport and treated above ground.

SVE appears to have very limited applications for DNAPLs and aqueous-phase contaminants in the saturated zone. Molecular diffusion dominates vertical dispersion of VOCs from the capillary fringe and saturated zone. As a consequence, low mass transfer rates limit the mass of VOC which can be removed by SVE from ground water. Steep vertical concentration gradients develop, but the amount of mass transferred from the saturated zone to the unsaturated zone is minimal.

5.6 Bioremediation

The applicability of bioremediation first depends on the inherent biodegradability of the specific contaminant. The inherent biodegradability of the individual constituents of DNAPLs varies widely. Certain nonchlorinated, low-molecular weight contaminants are readily biodegraded under aerobic conditions. The biodegradability of high-molecular weight contaminants such as PCBs and the highly condensed polyaromatic hydrocarbons present in creosote is limited by their solubility and non-bioavailability. Effective biodegradation of chlorinated solvents and PCBs could require both an anaerobic dechlorination step and an aerobic step in which a supplemental carbon source is provided.

The applicability of biodegradation for DNAPLs will also be limited by other factors. Bioremediation in the saturated zone requires delivery of reagents required for biodegradation (e.g., oxygen or other electron acceptor, inorganic nutrients) to the contaminated zone. High contaminant concentrations in DNAPL zones will result in high stoichiometric reagent demands. Limitations on reagent delivery associated with advective transport of the dissolved reagents into the contaminated zone will challenge the practicality of bioremediation in terms of the required delivery rate of reagent-enriched ground water and/or the duration of bioremediation. The high concentrations of toxic compounds in some DNAPLs may also be inhibitory or toxic to microbial activity.

Due to the toxicity of most DNAPLs, and the lack of essential nutrients, electron acceptors, and other requirements for life in the NAPL pool itself, the potential for biologically-mediated degradation of DNAPLs is limited. Bioremediation may be most appropriate as a "polishing step" following methods such as free-phase liquid removal or in situ flushing that remove the majority of the DNAPL. Bioremediation may also be more applicable for remediation of plumes of contaminated ground water emanating from DNAPL zones. In these cases, bioremediation may be more effective than a pump-and-treat remediation approach due to more aggressive removal of contaminants sorbed to the aquifer matrix or present in small amounts of DNAPL. However, bioremediation will often be subject to some of the same factors that limit the effectiveness of pump-and-treat or other in situ approaches (e.g., preferred flow paths resulting from subsurface heterogeneities). There are a limited number of field-scale tests that have been conducted recently, or are under way, that are defining the applicability of the technology at DNAPL sites. Numerous bench-scale research studies are also being conducted.

5.7 Treatment Train

If the intent of a remedial program at a DNAPL site is to restore an aquifer to its pre-contamination condition within a reasonable time span, more than one remedial technique may be required. An example of a treatment train presented at the workshop was a wood preserving site. It should be noted that despite the use of multiple techniques which resulted in significant DNAPL mass removal at this site, restoration has not been achieved in the pilot test area.

The facility treated railroad ties and other wood products for almost 100 years. Wood-preserving agents used in the operations included a creosote oil and asphalt-based petroleum oil mixture and pentachlorophenol. Approximately 100 acres of the site are contaminated with DNAPL in the underlying alluvial sands and gravels. Both nonaqueous and aqueous-phase contaminants were discharging through the alluvium into a nearby river.

A bentonite slurry wall was constructed around the site and drain lines were installed inside and outside the wall to maintain an inward and upward hydraulic gradient inside the containment area. Subsequently, a pilot program was initiated to evaluate a series of in situ treatment methods at the site. Selected remedial techniques included induced gradient product recovery using a dual drainline, chemically-enhanced in situ soil flushing, and in situ bioremediation.

The induced gradient recovery method was designed to significantly reduce the total mass of contaminant to levels conducive to cleanup by enhanced oil recovery techniques. Following product recovery efforts, a site-specific, chemically-enhanced in situ soil flushing method was applied. Surfactant, polymer, and alkaline agents were delivered to the subsurface to mobilize the remaining oily wastes, further reducing the subsurface DNAPL mass. The final step of the pilot program was in situ bioremediation. The naturally-occurring microbial populations were stimulated with supplied oxygen. Despite the apparent success of these techniques in

removing a large DNAPL mass, significant amounts of residual DNAPL remained in the test area.

At this site, numerous remedial technologies were employed both in parallel and in series. Currently, it appears this type of treatment train may be required to potentially restore DNAPL-contaminated sites. However, there are many technological and conceptual problems with present-day remedial systems that require extensive research, development, and demonstration. Implementation and successful use on large scales may not be achievable. Even at sites where several emerging technologies have been applied, they have not been fully successful at removing DNAPL. Nevertheless, groundwater remediation is a relatively new science and as emerging technologies evolve to proven technologies, significant advances in DNAPL remediation can be anticipated.

This document was edited by Steven D. Acree, Randall R. Ross, and Marion R. Scalf of U.S. EPA Robert S. Kerr Environmental Research Laboratory, Ada, OK, Ellen R. Graber of U.S. EPA Region VI, on temporary detail at RSKERL, and James W. Mercer and Robert M. Cohen of GeoTrans, Inc.

Table 1. Summary of Remedial Operations Potentially Applicable at DNAPL Contamination Sites.

METHOD	APPLICATION	PROCESS	EFFECTIVENESS / ADVANTAGES / LIMITATIONS	EXPERIENCE	REFERENCES
Hydraulic Containment	Hydraulic containment is used to prevent the undesired migration of chemicals through the saturated zone	Hydraulic containment of dissolved chemicals may be achieved by pumping groundwater from wells and/or drains. Full horizontal and vertical hydraulic containment of DNAPL has not been demonstrated in the field. Fluid flow control can be augmented by injecting water through wells and/or drains, and by the installation of physical barriers (cut-off walls and landfill covers). Monitor wells are utilized to determine whether or not the specified hydraulic gradients have been obtained and chemical migration has been arrested.	Long-term hydraulic containment will be needed at many DNAPL sites because residual and trapped pools of DNAPL are long-term sources of groundwater contamination. The effectiveness of a hydraulic containment system depends largely on the adequacy of the design and operation of the system. Containment is eased where there is a continuous barrier layer that prevents downward DNAPL migration. It is theorized that downward migration may be arrested at some sites by creating an upward hydraulic gradient into the DNAPL zone that exceeds the density difference between DNAPL and water. Vertical hydraulic containment of DNAPL, however, has yet to be demonstrated in the field. The main drawbacks to hydraulic containment systems are cost and the need for long-term operation.	The components of a hydraulic containment system (wells, drains, cut-off walls, and covers) have been widely used for contamination site remediation and other applications. Although hydraulic containment is generally a proven migration control technology, its success depends on adequate design and implementation.	Cherry et al. (1990), Cohen et al. (1987), Mackay and Cherry (1989), Mercer et al. (1990)
Containment Using Physical Barriers	Capillary and low permeability barriers (fine-grained walls) can be constructed to limit NAPL migration in the saturated zone	Low permeability, fine-grained barrier walls (i.e., slurry walls, concrete walls, sheet piling with grouted joints, etc.) can be constructed to impede the lateral migration of non-wetting DNAPL below the water table. Where possible, barrier walls should be keyed into a low permeability, capillary barrier layer beneath the DNAPL contamination zone.	Barrier walls can provide cost-effective control over NAPL migration in favorable settings. Barrier walls have not been tested, however, to determine their capacity for long-term impedance of NAPL migration. Small fractures or openings will facilitate DNAPL breakthrough. The long-term integrity of engineered subsurface barriers is not well-known. Consideration must be given to the compatibility of barrier wall materials with subsurface chemicals, the potential for inducing migration during wall construction, and changes to the hydrogeologic system effected by wall emplacement.	Cutoff walls have been installed as part of containment systems at many sites.	Cherry et al. (1990), Sale et al. (1988)

Table 1. Summary of Remedial Operations Potentially Applicable at DNAPL Contamination Sites (continued).

METHOD	APPLICATION	PROCESS	EFFECTIVENESS / ADVANTAGES / LIMITATIONS	EXPERIENCE	REFERENCES
Product Recovery by Pumping	Mobile NAPL can be pumped from wells or drains.	Mobile NAPL can be pumped from wells and drains utilizing single pumps to extract total fluids or NAPL only, or using individual pumps to withdraw water and NAPL separately.	Wells should be placed in stratigraphic and structural traps to optimize recovery where NAPL pools are present. Long-term recovery is increased by maintaining a maximum thickness and saturation of NAPL adjacent to the well. This can be achieved by pumping NAPL and water separately. Pumping water above a DNAPL pool causes DNAPL upwelling which works to increase the formation transmissivity to DNAPL flow. A dual pumping system can be operated using wells or drains. Overpumping the NAPL may result in truncation of the NAPL layer at the well edge and significantly reduce the formation transmissivity to NAPL flow. Pumping may cause NAPL to enter previously uncontaminated sections, thereby enlarging the contaminated zone. In shallow, unconfined formations, it will generally not be possible to significantly diminish the NAPL residual saturation by increasing hydraulic gradients alone. Pumping can be used to remove mobile NAPL and reduce the potential for continued NAPL migration, however. Vacuum-enhanced pumping may be a way to increase gradients for improved mobilization and hydraulic control.	A great deal of experience has been acquired by the oil industry pumping LNAPL from crude oil reservoirs and by the environmental industry pumping petroleum products from contaminated shallow formations. Little documentation is available, however, regarding DNAPL product recovery at contamination sites.	Blake et al. (1990), Ferry et al. (1986), McWhorter (1991), Newell and Connor (1991), Sale et al. (1988 and 1989), Sale and Piontek (1988), Schmidtke et al. (1987), Villaume (1991), Wisniewsky et al. (1985)
EOR using Water Flooding	Waterflooding can be used to increase the recovery of NAPL from the saturated zone.	Referred to as secondary recovery by the oil industry, waterflooding involves the injection of water in wells or drains to hydraulically sweep NAPL toward production wells. Recovery can be enhanced because injection/ extraction systems (i.e., line-drive and five spot systems) allow for the development and sustenance of increased hydraulic gradients and flow rates, elimination of dead zones, and overall improved flow control management.	Refer to the soil flushing comments.	Although routinely utilized for secondary recovery by the oil industry, waterflooding has been utilized to recover NAPL at only a few environmental contamination sites.	Anderson (1987c), Donaldson et al. (1989), Newell and Connor (1991), Rathmell et al. (1973), Sale and Piontek (1988), Sale et al. (1989), Sale et al. (1988)

Table 1. Summary of Remedial Operations Potentially Applicable at DNAPL Contamination Sites (continued).

METHOD	APPLICATION	PROCESS	EFFECTIVENESS / ADVANTAGES / LIMITATIONS	EXPERIENCE	REFERENCES
Soil Flushing by Flooding with Water, Steam, Surfactants, Alkaline Agents, Polymers, and Cosolvents [see specific flood EOR technologies below]	In situ soil flushing can be used to enhance recovery of NAPLs, adsorbed chemicals, and dissolved chemicals from the saturated or unsaturated zone.	Injection wells or drains, or surface application delivery systems are used to flood the contaminated zone with flushing solutions and sweep the contaminants to recovery wells or drains (i.e., surfactants, cosolvents, alkaline agents, polymers, steam, etc.). Drains are typically used to effect line-drive sweeps; wells are typically used to effect line-drive or five-spot sweeps. The flood enhances recovery of NAPL by reducing interfacial tension, reducing NAPL viscosity, lowering the mobility ratio, increasing solubility, and/or increasing hydraulic gradients (i.e. raising the capillary number). Recovery of adsorbed and/or dissolved chemicals is also enhanced by these processes. Displaced NAPL and chemicals are recovered by pumping wells and/or drains. At the conclusion of the flood, the flushing solution can be displaced to the recovery system by injecting water via the delivery system. Soil flushing may be used as an intermediate process in a train of remedial measures.	Soil flushing is most effective in permeable, uniform media. It can be used to speed the removal of contaminants from the subsurface. Heterogeneous and low permeability soils will generally result in reduced sweep efficiency, longer project duration, and less successful recovery. Soil flushing can, however, be used to reduce the NAPL residual saturation to levels below the immobile saturation at ambient site conditions. The movement of contaminants mobilized by the flood must be carefully controlled to prevent detrimental migration. Consideration must also be given to: the toxicity and fate of the flushing solution and potential adverse reactions (permeability reduction, impairment of biodegradation rates, etc.) caused by the solution. Site-specific bench and pilot-scale field tests are generally recommended prior to implementation of a field-scale remedial project. The site-specific application of EOR methods may prove to be effective within a train of treatment measures to remediate NAPL-contaminated sites.	Although the oil industry has made extensive use of flooding technology to enhance oil recovery, few in-situ soil flushing operations have been conducted at contamination sites. In general, the application of soil flushing technologies to remediate contamination sites is at the pilot-test stage and the effectiveness of these technologies in environmental applications is unknown.	Sims (1990), USEPA (1990a and 1990b) [see specific flooding technologies below]
EOR Using Surfactant Water Flooding	Surfactant flooding can be used to increase NAPL recovery during a flood operation in the saturated zone.	Surfactant solution is injected as a slug in a flooding sequence to decrease the interfacial tension between NAPL and water by several orders of magnitude (i.e., from 20-50 dynes/cm to less than 0.01 dynes/cm). The development of ultra-low interfacial tension effects a commensurate 3-5 orders-of-magnitude increase in the capillary number (N_{ca}) which is the ratio of viscous to capillary forces, sometimes expressed as $N_{ca}=\mu v/\sigma\phi$, where μ and v are the viscosity and Darcy velocity of the displacing fluid, σ is the interfacial tension, and ϕ is the porosity. Ultra-low interfacial tension and higher capillary numbers improve the NAPL displacement efficiency of a flood, promote the coalescence of NAPL ganglia and development of a NAPL bank in front of the surfactant slug, and result in increased NAPL recovery and reduced NAPL residual saturation. Surfactant flooding can also enhance NAPL recovery by causing increased NAPL wetting, solubilization, and emulsification. Some surfactants used in EOR operations by the oil industry include petroleum sulfonates, synthetic sulfonates, ethoxylated sulfonates, and ethoxylated alcohols.	The high cost of surfactant chemicals has limited the commercial application of surfactant flooding by the oil industry. Using surfactant solutions to enhance NAPL recovery at contamination sites, however, may be more attractive given the higher costs associated with waste site remediation. At many sites, reducing interfacial tension will be the only practical way to mobilize residual NAPL. Refer to the soil flushing comments.	There were approximately 30 active EOR field-scale projects using surfactant injection in the United States in 1980. Application of surfactant flooding by the oil industry for EOR is limited by its high cost relative to other EOR methods. The application of surfactant flooding to enhance NAPL recovery at contamination sites is in its infancy. Surfactants were included in a soil flushing solution of alkaline, polymer, and surfactant agents (A-P-S) to enhance DNAPL recovery at the Laramie Tie Plant.	Akstinat (1981), Beikirch (1991), Donaldson et al. (1989), Ellis et al (1985), Flumerfelt et al (1981), Fountain (1991), Gogarty (1983), Hesselink and Faber (1981), Manji and Stasiuk (1988), Nash (1988), Nelson (1989), Nelson et al. (1984), Neustadter (1984), Novosad (1981), Pitts et al. (1989), Salagar et al. (1979), Shah (1981), Sharma and Shah (1989) Tuck et al. (1988)

Table 1. Summary of Remedial Operations Potentially Applicable at DNAPL Contamination Sites (continued).

METHOD	APPLICATION	PROCESS	EFFECTIVENESS / ADVANTAGES / LIMITATIONS	EXPERIENCE	REFERENCES
EOR Using Alkaline Water Flooding	Alkaline flooding can be used to increase NAPL recovery during a flood operation.	Alkaline waterflooding is an EOR process where inexpensive caustics such as sodium carbonate, sodium silicate, sodium hydroxide, and potassium hydroxide are mixed with the injection water. The alkaline agents raise the pH of the flood and react with organic acids that are present in oil. This reaction generates surfactants at the oil-water interface and leads to improved oil recovery due to (1) greatly reduced interfacial tension, (2) emulsification effects, and (3) wettability reversals, which can mobilize entrapped oil ganglia. Alkaline waterflooding may be used in conjunction with other EOR methods; for example, it is reported to be an effective preflush for surfactant-polymer floods.	NAPLs must have acidic components to react with the alkali agents to form surfactants. Alkaline flooding is relatively cheap compared to some other EOR methods, but alkali consumption due to reaction with porous media may be a limiting factor. Refer to the soil flushing comments.	Numerous alkaline waterflood EOR projects have been conducted by the oil industry (approximately 40 were reported begun in the U.S between 1979 and 1981) The application of alkaline flooding to enhance NAPL recovery at contamination sites is in its infancy. Alkaline agents were included in a soil flushing solution of alkaline, polymer, and surfactant agents (A-P-S) to enhance DNAPL recovery at the Laramie Tie Plant.	Breit et al. (1981), Campbell (1981), Castor et al. (1981b), Donaldson et al. (1989), Janssen-VanRosmalen and Hesselink (1981), Kumar et al. (1989), Mayer et al. (1983), Nelson et al (1984), Pitts et al. (1989), Sale et al. (1989), Surkalo (1990)
Polymer Water Flooding	Polymer flooding can be used to increase NAPL recovery during a flood operation in the saturated zone.	Polymers are large molecules that can be dispersed in a waterflood to increase the viscosity of the flood, thereby reducing the mobility ratio and improving the volumetric sweep efficiency (NAPL recovery). The mobility ratio is defined as the mobility of the displacing fluid (effective permeability/viscosity for water) divided by the mobility of the displaced fluid (effective permeability/viscosity for NAPL). Lower mobility ratios favor NAPL displacement and recovery. An effective polymer will impart a high viscosity at low concentration. Only two types of polymers are commonly used by the oil industry (polyacrylamides and polysaccharides). In EOR operations, polymer flooding is often used as part of a phased injection sequence consisting of: (1) a preflush to adjust the pH and salinity of the reservoir; (2) surfactants and/or alkaline agents to reduce interfacial tension; (3) polymer solution to increase viscosity and improve displacement efficiency, and (4) waterflood to displace the mobilized oil and EOR solutions.	The advantage of polymer flooding is that it improves the volumetric sweep efficiency of a water flood process. By itself, polymer flooding will not, however, mobilize trapped residual NAPL in a water-wet situation. Potential limitations include: the risk of reduced injectivity caused by wellbore plugging, increased project durations and slowed recovery due to the lower absolute flood mobility, polymer degradation, excessive cost. Refer to the soil flushing comments.	Polymer flooding had been initiated at about 180 field-scale EOR projects in the U S. by the mid 1980s. There is debate in the oil industry, however, regarding whether or not polymer flooding by itself provides more than a small incremental recovery. The application of polymer flooding to enhance NAPL recovery at contamination sites is in the early development stage. Polymers were used in a soil flushing solution of alkaline, polymer, and surfactant agents (A-P-S) to enhance DNAPL recovery at the Laramie Tie Plant.	Caenn et al. (1989), Castor et al. (1981a), Chauveteau and Zaitoun (1981), Donaldson et al. (1989), Hesselink and Faber (1981), Labastie and Vio (1981), Lin et al. (1987), Littman (1988), Pitts et al. (1989), Sale et al. (1989), Shah (1981), Surkalo et al. (1986), Yen et al. (1989)

Table 1. Summary of Remedial Operations Potentially Applicable at DNAPL Contamination Sites (continued).

METHOD	APPLICATION	PROCESS	EFFECTIVENESS / ADVANTAGES / LIMITATIONS	EXPERIENCE	REFERENCES
EOR using Chemi-cally-Enhanced Dissolution (Cosolvents)	Cosolvents can be used to increase the dissolution and recovery of NAPL and adsorbed chemicals from the subsurface.	Cosolvents injected into a contamination zone via wells or drains increase the dissolution of NAPLs and adsorbed chemicals. Continued flooding of the contamination zone with cosolvents or another flood (water, polymers, etc.) drives the elutriate to production wells or drains. The elutriate may be treated and recycled through the system.	Refer to the soil flushing comments.	Miscible flooding with carbon dioxide and/or hydrocarbon solvents has been tested at numerous sites for EOR by the oil industry. Several bench- and pilot-scale studies have been conducted on in-situ cosolvent flushing technology at contamination sites with variable success.	Blackwell (1981), Fountain (1991), Groves (1988), McDermott et al. (1988), Mehdizadeh et al. (1989), Nash (1987), Nash and Traver (1986), Rao et al. (1991), Roy and Griffon (1988), Sayegh and McCaffery (1981), Taber (1981), USEPA (1990a and 1990b)
EOR Using Thermal Methods (Steam or Hot Water Flooding)	Thermal methods (steam or hot water flooding) can be used to increase NAPL recovery.	High-temperature steam is injected via wells into the contamination zone. The steam yields heat to the formation and condenses into a zone that acts as a hot water flood. Coupled with the continuous injection of steam behind it, this hot water drives NAPL to the recovery wells. NAPL recovery is enhanced because: (1) the NAPL becomes less viscous and more mobile upon heating; (2) NAPL solubility may be increased by the higher temperatures; (3) volatile NAPL vaporizes, moves ahead of the hot water and then condenses to form a NAPL bank; and, (4) the increased NAPL saturation in the NAPL condensate bank provides increased NAPL transmissivity and, under favorable conditions, results in a snowball effect.	The application of thermal methods to enhance DNAPL recovery at contamination sites may become more popular based on the successful use of steam injection by the oil industry, the encouraging results of limited lab and pilot-scale testing of steam injection for DNAPL recovery, and the fact that additional chemicals need not be injected to recover the contaminants. Heating may convert DNAPL to LNAPL, thereby promoting mobility due to buoyancy forces. Costs may be high due to heat loss and the need to heat large volumes of subsurface materials. Refer to the soil flushing comments.	There were approximately 200 active thermal EOR projects in the United States in 1986. Steam and hot water displacement of NAPLs at contamination sites has been evaluated in a few laboratory and pilot field studies.	Blevin et al. (1984), Boberg (1988), Donaldson et al. (1989), Doscher and Ghassemi (1981), Goyal and Kumar (1989), Hunt et al. (1988a and 1988b), Leuschner and Johnson (1990), Mandl and Volek (1969), Menegus and Udell (1985), Miller (1975), Offeringa et al. (1981), Prats (1989), USEPA (1990b), Volek and Pryor (1972), Willman et al. (1961), Yortsos and Gavalas (1981)
Pump-and-Treat	Dissolved chemicals can be removed from the saturated zone by pumping groundwater.	Contaminated groundwater is pumped from wells or drains using conventional technology. Recovery rates can be optimized by fine-tuning pumping rates, well locations, etc.	Pump-and-treat is typically utilized as part of a hydraulic containment or aquifer restoration program. DNAPL, where present, will be a long-term source of groundwater contamination. Due to the relatively low solubility of most DNAPLs, pumping and treatment is generally not efficient in removing DNAPL from the subsurface.	Recovery of dissolved chemicals by ground-water pumping is a widely-used, proven technology, but not for removal of NAPL.	Anderson et al. (1987, 1991a and 1991b), Anderson (1988), Feenstra and Cherry (1988), Hunt et al. (1988a), Johnson (1991), Johnson and Pankow (1991), Keely (1989), Mackay and Cherry (1985), Mercer et al. (1990), Mercer and Cohen (1990), Schwille (1988)

Table 1. Summary of Remedial Operations Potentially Applicable at DNAPL Contamination Sites (continued).

METHOD	APPLICATION	PROCESS	EFFECTIVENESS / ADVANTAGES / LIMITATIONS	EXPERIENCE	REFERENCES
Vacuum Extraction (VE)	VE may be used to remove volatile chemicals from the unsaturated zone and to prevent uncontrolled migration of volatile chemicals in soil gas. If the water table is lowered, VE may be used to remove residual NAPL from below the original water table elevation.	Using unsaturated zone wells equipped with blowers or vacuum pumps, air is forced through soils contaminated with volatile chemicals. The air flow generates advective vapor fluxes that change the vapor-liquid equilibrium, inducing volatilization of contaminants. The resulting vapors are collected and treated. Positive differential pressure systems induce vapor flow away from the control points and negative differential pressure systems induce vapor flow toward control points. Experience had demonstrated that generation of negative differential gas pressures typically provides the most favorable field results.	Vacuum extraction is most effective removing low molecular weight, volatile chemicals (dimensionless Henry's Law Constant > 0.01) from homogeneous, permeable media. Intermittent vacuum extraction operation is generally more efficient than constant operation. Vacuum extraction systems can be installed using off-the-shelf components and conventional drilling methods. Vacuum extraction is less effective at removing volatile chemicals from heterogeneous and low permeability soils and is ineffective removing volatile chemicals from the saturated zone. Because it induces water table upwelling, vacuum extraction can result in groundwater contamination where chemicals are located just above the water table. Groundwater recovery wells located adjacent to vacuum extraction wells may be necessary. Alternatively, lowering the water table to allow volatile chemical recovery by vacuum extraction may promote DNAPL remobilization and sinking.	In-situ vacuum extraction processes have been employed at more than 100 contamination sites in the United States.	Agrelot et al. (1985), Ardito and Billings (1990), Baehr et al. (1989), Batchelder et al. (1986), Blake et al. (1990), Blake and Gates (1986), Crow et al. (1985 and 1987), DiGiulio and Cho (1990), Dunlap (1984), Gierke et al. (1990), Hutzler et al. (1989), Johnson et al. (1988), Johnson et al. (1990a and 1990b), Jury et al (1990), Krishnayya et al. (1988), Mackay et al. (1990), Marley and Hoag (1984), Massmann (1989), McClellen and Gillham (1990), O'Connor et al. (1984), Rathfelder (1989), Rathfelder et al. (1991), Regalbuto et al. (1988), Sims (1990), Stephanatos (1988), Texas Research Inst (1984), Thornton and Wootan (1982), Wilson et al (1987), USEPA (1989a, 1990a and 1990b)
Steam and Hot Air Injection to Enhance Vacuum Extraction	Vacuum extraction in the unsaturated zone can be enhanced by steam and hot air injection.	Steam or hot air injected into or below the zone of soil contamination can improve the effectiveness of vacuum extraction systems. Heating and increased soil gas movement caused by steam and hot air injection raise the vaporization rate of volatile and some semi-volatile compounds. Additionally, contaminated soil water and low viscosity NAPLs can be physically displaced by the condensate that forms in front of the steam zone.	In general, steam or hot air injection will increase the effectiveness of a vacuum extraction system. Heating will reduce the viscosity and interfacial surface tension of residual or trapped DNAPL in the unsaturated zone, which may result in uncontrolled migration. Similarly, accumulation of DNAPL at the steam condensate front may result in uncontrolled downward or lateral migration of the DNAPL.	Successful laboratory and pilot-scale field studies have been conducted using steam and hot air stripping to enhance vacuum extraction recovery of solvents and petroleum contaminants from soil. Two different systems have been used: (1) a mobile unit consisting of a hollow stem auger rig outfitted for steam/air injection and vacuum extraction of vapors, and (2) a fixed system of injection and extraction wells.	Baum (1988), Hunt et al. (1988b), DePauli (1990), de Percin (1990), Houthoofd et al. (1991), Hinchee and Smith (1990), Johnson and Guffey (1990), Lord et al (1988, 1989, 1990, and 1991), Nunno et al. (1989), Udell and Stewart (1989 and 1990), USEPA (1990a and 1990b)

Table 1. Summary of Remedial Operations Potentially Applicable at DNAPL Contamination Sites (continued).

METHOD	APPLICATION	PROCESS	EFFECTIVENESS / ADVANTAGES / LIMITATIONS	EXPERIENCE	REFERENCES
Radio Frequency Heating (RFH) to Enhance Vacuum Extraction	Vacuum extraction of chemicals that volatilize in the temperature range of 80° to 300° C can be enhanced by using radio frequency heating of contaminated soil.	In situ radio frequency heating (RFH) involves heating soil with electromagnetic energy in the radio frequency band (typically 6.7 MHz to 2.5 GHz). Using a modified radio transmitter as a power source, energy is transmitted to the zone targeted for decontamination via electrodes placed in an array of boreholes. This energy heats the soil to temperatures between 150° and 300° C. Volatilized chemicals are recovered with soil gas for treatment by applying a vacuum to selected hollow electrodes. A rubber sheet barrier may be spread over the soil surface to provide thermal insulation and prevent fugitive emissions	In general, RFH will increase the effectiveness of a vacuum extraction system. The technology is only applied to the unsaturated zone and its use is precluded where buried metal objects are present. As with vacuum extraction, this method is best suited to sites where volatile chemicals are present at shallow depth in homogeneous, coarse-grained soils. The uniformity of heating provided by RFH (which occurs due to dielectric heating mechanisms rather than the thermal conductivity of the soil), however, may result in more uniform decontamination than achieved using steam or hot air injection methods and may make this method more applicable to heterogeneous soils. Heating will reduce the viscosity and possibly the interfacial surface tension of residual or trapped DNAPL in the unsaturated zone, which may result in uncontrolled migration	Several bench- and pilot-scale tests and limited field-scale testing have been conducted using RFH to remove 70% to 99% of various solvents, jet fuel, and PCBs from shallow soils. Although RFH continues to be in the pilot- and field scale demonstration stage, at least one company has announced the availability of RFH on a commercial basis	Dev (1986), Dev et al (1988), Dev and Downey (1989), Houthoofd et al (1991), Sims (1990), Sresty et al.(1986), USEPA (1990)
Bioreme-diation	Bioremediation involves enhancement of natural processes to degrade hazardous chemicals in the subsurface.	Naturally occurring microbes can be used to degrade and/ or detoxify hazardous chemicals in the subsurface. Bioremediation approaches include: (1) stimulation of biochemical mechanisms for degrading chemicals; (2) enhancement by delivery of exogeneous acclimated or specialized microorganisms; (3) delivery of cell-free enzymes; and (4) vegetative uptake. Typically, oxygen and nutrients are delivered to the contamination zone via wells and/or drains to increase the rate of aerobic biodegradation.	Adequate characterization of the hydraulic conductivity distribution is necessary to achieve efficient delivery of oxygen, nutrients, and/or microbes within the contaminated zone. Many NAPLs are toxic to microbes and/or resistant to biodegradation. As a result, degradation may be limited to the periphery of NAPL contamination zones or to the aqueous phase. Degradation may generate other undesirable chemicals. Bench and pilot studies are recommended Bioremediation is typically used as a "polishing" step with limited mass removal following the application of other chemical recovery and treatment processes	Efforts to stimulate biodegradation have been employed at full field-scale at numerous contamination sites with varying degrees of success and documentation	Downey (1990), Hinchee (1989), Hinchee et al (1990), Leuschner and Johnson (1990), Lokke (1984), Novak et al (1984), Jhaveri and Mazzacca (1983), Lee et al (1988), Lee and Ward (1984), Kuhn et al (1985), Miller et al (1990), Piontek et al (1989), Raymond (1974), Sims (1988), Sims (1990), Suflita and Miller (1985), USEPA (1990a and 1990b), Vogel et al. (1987), Wilson et al. (1986), Wilson and Rees (1985), Yaniga and Mulry (1984)
In-Situ Aeration in the Saturated Zone (Air Sparging and UVB Wells)	Air stripping can be applied below the water table to remove volatile contaminants from the saturated zone.	Volatile contaminants below the water table can be stripped by injecting air through wells. Vaporized volatiles move with the air to the unsaturated zone and are recovered using a vacuum extraction system. Another in-situ groundwater stripping process is known as the Underpressure-Vaporizer-Well (UVB) method in which contaminated groundwater is stripped by air at negative pressures in a special filtered well. The contaminated gas is collected and treated at the well head.	In-situ air injection will be most effective removing low molecular weight, volatile compounds. Little documentation is available regarding the effectiveness, advantages or limitations of air sparging and UVB wells.	The application of in-situ air stripping of groundwater is very limited. The UVB Well method is currently in use at several sites in Germany.	Blake et al (1990), Herrling et al. (1990), Herrling and Buermann (1990)

Table 1. Summary of Remedial Operations Potentially Applicable at DNAPL Contamination Sites (concluded).

METHOD	APPLICATION	PROCESS	EFFECTIVENESS / ADVANTAGES / LIMITATIONS	EXPERIENCE	REFERENCES
Containment by Solidification, Stabilization, and/or In-Situ Vitrification	Solidification, stabilization, and in-situ vitrification are used to immobilize subsurface contaminants.	Waste solidification involves mixing cementing agents with soil to mechanically bind subsurface contaminants and thereby reduce their rate of release. Cementing agents (such as pozzolan-portland cement, lime-flyash pozzolan, and asphalt systems) can be combined with contaminated soils by injection, in-situ mechanical mixing, or above ground mechanical mixing. During waste stabilization, reagents are used to convert contaminants to their least toxic, soluble, or mobile form In-situ vitrification utilizes an electrical network (125 or 138kV) to melt contaminated soils and sludges at temperatures of 1600 to 2000° C. Electricity is transmitted from a power source into contaminated soil via large electrodes. Organic contaminants are pyrolized and inorganic contaminants are incorporated within the vitrified mass. Vapors can be captured at the surface for treatment. Obtaining complete and uniform mixing of the solidifying and/or stabilizing agents with the contaminated soil is a critical factor determining the success of solidification/ stabilization systems.	Successful application of these methods becomes more difficult with increasing depth and with increasing water content. Costs are high, but may be competitive with other remedies. Bench studies and pilot field tests are generally necessary. Mixed, complex wastes present special challenges. Volatilization, mobilization, and migration of contaminants may be caused by these processes. The long-term stability and leaching characteristics of contaminated materials that have been solidified, stabilized or vitrified is unknown.	Several different solidification-stabilization processes have undergone pilot tests and full-scale field demonstrations. Six full-scale demonstrations of in-situ vitrification have been conducted at the DOE Hanford site, and more than 90 in-situ vitrification tests of various scales have been conducted on PCB wastes, and other solid combustibles and liquid chemicals.	Cullinane et al. (1986), Fitzpatrick et al. (1986), Sims (1990), USEPA (1990a and 1990b)
Excavation	Excavation is used to remove contaminated materials from the subsurface.	Conventional excavating methods are used to remove contaminated materials from the subsurface for subsequent incineration, treatment and/or disposal.	Excavation can be a very effective site remedy where contaminant penetration is limited to shallow soils and where shallow contamination hot spots are identified. The cost and difficulty of excavation increases with the depth of contaminant migration and generally becomes prohibitive in bedrock. Additional concerns include potential fugitive dust, liquid, and gas emissions caused by excavating contaminated materials, and the possibility that DNAPL may have migrated beneath the excavation limit, thereby reducing the effectiveness of excavation as a remedy. Saturated zone difficulties include dewatering.	Excavation of contaminated materials is a widely-used remedy of proven value in appropriate situations.	

Appendix A

Dense Nonaqueous Phase Liquids, a USEPA Ground-Water Issue Paper

United States Environmental Protection Agency | Office of Research and Development | Office of Solid Waste and Emergency Response | EPA/540/4-91-002 March 1991

EPA Ground Water Issue

DENSE NONAQUEOUS PHASE LIQUIDS

Scott G. Huling* and James W. Weaver**

Background

The Regional Superfund Ground Water Forum is a group of EPA professionals representing EPA's Regional Superfund Offices, committed to the identification and the resolution of ground water issues impacting the remediation of Superfund sites. The Forum is supported by and advises the Superfund Technical Support Project. Dense nonaqueous phase liquids is an issue identified by the Forum as a concern of Superfund decision-makers. For further information contact Scott G. Huling (FTS:743-2313), Jim Weaver (FTS:743-2420), or Randall R. Ross (FTS: 743-2355).

Introduction

Dense nonaqueous phase liquids (DNAPLs) are present at numerous hazardous waste sites and are suspected to exist at many more. Due to the numerous variables influencing DNAPL transport and fate in the subsurface, and consequently, the ensuing complexity, DNAPLs are largely undetected and yet are likely to be a significant limiting factor in site remediation. This issue paper is a literature evaluation focusing on DNAPLs and provides an overview from a conceptual fate and transport point of view of DNAPL phase distribution, monitoring, site characterization, remediation, and modeling.

A nonaqueous phase liquid (NAPL) is a term used to describe the physical and chemical differences between a hydrocarbon liquid and water which result in a physical interface between a mixture of the two liquids. The interface is a physical dividing surface between the bulk phases of the two liquids, but compounds found in the NAPL are not prevented from solubilizing into the ground water. Immiscibility is typically determined based on the visual observation of a physical interface in a water- hydrocarbon mixture. There are numerous methods, however, which are used to quantify the physical and chemical properties of hydrocarbon liquids (31).

Nonaqueous phase liquids have typically been divided into two general categories, dense and light. These terms describe the specific gravity, or the weight of the nonaqueous phase liquid relative to water. Correspondingly, the dense nonaqueous phase liquids have a specific gravity greater than water, and the light nonaqueous phase liquids (LNAPL) have a specific gravity less than water.

Several of the most common compounds associated with DNAPLs found at Superfund sites are included in Table 1. These compounds are a partial list of a larger list identified by a national screening of the most prevalent compounds found at Superfund sites (65). The general chemical categories are halogenated/non-halogenated semi-volatiles and halogenated volatiles. These compounds are typically found in the following wastes and waste-producing processes: solvents, wood preserving wastes (creosote, pentachlorophenol), coal tars, and pesticides. The most frequently cited group of these contaminants to date are the chlorinated solvents.

DNAPL Transport and Fate - Conceptual Approach

Fate and transport of DNAPLs in the subsurface will be presented from a conceptual point of view. Figures have been selected for various spill scenarios which illustrate the general behavior of DNAPL in the subsurface. Following the conceptual approach, detailed information will be presented explaining the specific mechanisms, processes, and variables which influence DNAPL fate and transport. This includes DNAPL characteristics, subsurface media characteristics, and saturation dependent parameters.

Unsaturated Zone

Figure 1 indicates the general scenario of a release of DNAPL into the soil which subsequently migrates vertically under both the forces of gravity and soil capillarity. Soil capillarity is also responsible for the lateral migration of DNAPL. A point is reached at which the DNAPL no longer holds together as a continuous phase, but rather is present as isolated residual globules. The fraction of the hydrocarbon that is retained by capillary forces in the porous media is referred to as residual

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Director

Table 1. Most prevalent chemical compounds at U.S. Superfund Sites (65) with a specific gravity greater than one.

Compound	Density [1]	Dynamic[2] Viscosity	Kinematic Viscosity[3]	Water[4] Solub.	Henry's Law Constant[5]	Vapor[6] Pressure
Halogenated Semi-volatiles						
1,4-Dichlorobenzene	1.2475	1.2580	1.008	8.0 E+01	1.58 E-03	6 E-01
1,2-Dichlorobenzene	1.3060	1.3020	0.997	1.0 E+02	1.88 E-03	9.6 E-01
Aroclor 1242	1.3850			4.5 E-01	3.4 E-04	4.06 E-04
Aroclor 1260	1.4400			2.7 E-03	3.4 E-04	4.05 E-05
Aroclor 1254	1.5380			1.2 E-02	2.8 E-04	7.71 E-05
Chlordane	1.6	1.1040	0.69	5.6 E-02	2.2 E-04	1 E-05
Dieldrin	1.7500			1.86 E-01	9.7 E-06	1.78 E-07
2,3,4,6-Tetrachlorophenol	1.8390			1.0 E+03		
Pentachlorophenol	1.9780			1.4 E+01	2.8 E-06	1.1 E-04
Halogenated Volatiles						
Chlorobenzene	1.1060	0.7560	0.683	4.9 E+02	3.46 E-03	8.8 E+00
1,2-Dichloropropane	1.1580	0.8400	0.72	2.7 E+03	3.6 E-03	3.95 E+01
1,1-Dichloroethane	1.1750	0.3770	0.321	5.5 E+03	5.45 E-04	1.82 E+02
1,1-Dichloroethylene	1.2140	0.3300	0.27	4.0 E+02	1.49 E-03	5 E+02
1,2-Dichloroethane	1.2530	0.8400	0.67	8.69 E+03	1.1 E-03	6.37 E+01
Trans-1,2-Dichloroethylene	1.2570	0.4040	0.321	6.3 E+03	5.32 E-03	2.65 E+02
Cis-1,2-Dichloroethylene	1.2480	0.4670	0.364	3.5 E+03	7.5 E-03	2 E+02
1,1,1-Trichloroethane	1.3250	0.8580	0.647	9.5 E+02	4.08 E-03	1 E+02
Methylene Chloride	1.3250	0.4300	0.324	1.32 E+04	2.57 E-03	3.5 E+02
1,1,2-Trichloroethane	1.4436	0.1190	0.824	4.5 E+03	1.17 E-03	1.88 E+01
Trichloroethylene	1.4620	0.5700	0.390	1.0 E+03	8.92 E-03	5.87 E+01
Chloroform	1.4850	0.5630	0.379	8.22 E+03	3.75 E-03	1.6 E+02
Carbon Tetrachloride	1.5947	0.9650	0.605	8.0 E+02	2.0 E-02	9.13 E+01
1,1,2,2-Tetrachloroethane	1.6	1.7700	1.10	2.9 E+03	5.0 E-04	4.9 E+00
Tetrachloroethylene	1.6250	0.8900	0.54	1.5 E+02	2.27 E-02	1.4 E+01
Ethylene Dibromide	2.1720	1.6760	0.79	3.4 E+03	3.18 E-04	1.1 E+01
Non-halogenated Semi-volatiles						
2-Methyl Napthalene	1.0058			2.54 E+01	5.06 E-02	6.80 E-02
o-Cresol	1.0273			3.1 E+04	4.7 E-05	2.45 E-01
p-Cresol	1.0347			2.4 E+04	3.5 E-04	1.08 E-01
2,4-Dimethylphenol	1.0360			6.2 E+03	2.5 E-06	9.8 E-02
m-Cresol	1.0380	21.0	20	2.35 E+04	3.8 E-05	1.53 E-01
Phenol	1.0576		3.87	8.4 E+04	7.8 E-07	5.293E-01
Naphthalene	1.1620			3.1 E+01	1.27 E-03	2.336E-01
Benzo(a)Anthracene	1.1740			1.4 E-02	4.5 E-06	1.16 E-09
Flourene	1.2030			1.9 E+00	7.65 E-05	6.67 E-04
Acenaphthene	1.2250			3.88 E+00	1.2 E-03	2.31 E-02
Anthracene	1.2500			7.5 E-02	3.38 E-05	1.08 E-05
Dibenz(a,h)Anthracene	1.2520			2.5 E-03	7.33 E-08	1 E-10
Fluoranthene	1.2520			2.65 E-01	6.5 E-06	E-02 E-06
Pyrene	1.2710			1.48 E-01	1.2 E-05	6.67 E-06
Chrysene	1.2740			6.0 E-03	1.05 E-06	6.3 E-09
2,4-Dinitrophenol	1.6800			6.0 E+03	6.45 E-10	1.49 E-05
Miscellaneous						
Coal Tar	1.028[7]	18.98[7]				
Creosote	1.05	1.08[8]				

[1] g/cc
[2] centipoise (cp), water has a dynamic viscosity of 1 cp at 20°C.
[3] centistokes (cs)
[4] mg/l
[5] atm-m³/mol
[6] mm Hg
[7] 45° F (70)
[8] 15 5°C, varies with creosote mix (62)

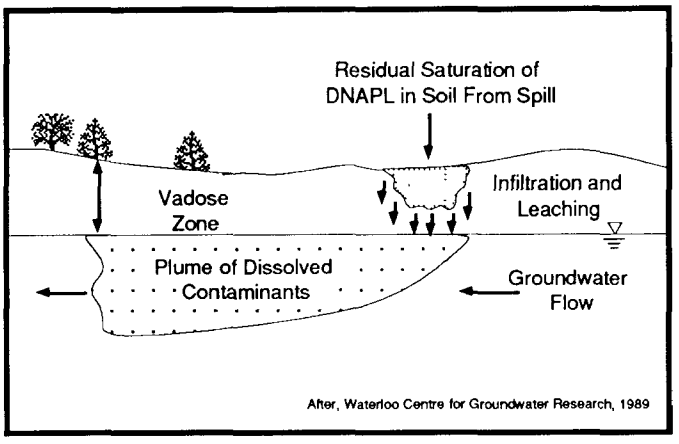

Figure 1. The entire volume of DNAPL is exhausted by residual saturation in the vadose zone prior to DNAPL reaching the water table. Soluble phase compounds may be leached from the DNAPL residual saturation and contaminate the ground water.

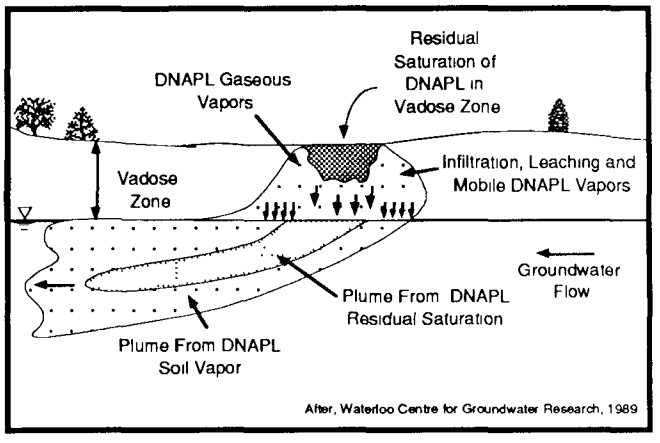

Figure 2. Migration of DNAPL vapors from the spill area and subsequent contamination of the soils and ground water.

saturation. In this spill scenario, the residual saturation in the unsaturated zone exhausted the volume of DNAPL, preventing it from reaching the water table. This figure also shows the subsequent leaching (solubilization) of the DNAPL residual saturation by water percolating through the unsaturated zone (vadose zone). The leachate reaching the saturated zone results in ground-water contamination by the soluble phase components of the hydrocarbon. Additionally, the residual saturation at or near the water table is also subjected to leaching from the rise and fall of the water table (seasonal, sea level, etc.).

Increasing information is drawing attention to the importance of the possibility that gaseous-phase vapors from NAPL in the unsaturated zone are responsible for contaminating the ground water and soil (18,47). It is reported that the greater "relative vapor density" of gaseous vapors to air will be affected by gravity and will tend to sink. In subsurface systems where lateral spreading is not restricted, spreading of the vapors may occur as indicated in Figure 2. The result is that a greater amount of soils and ground water will be exposed to the DNAPL vapors and may result in further contamination. The extent of contamination will depend largely on the partitioning of the DNAPL vapor phase between the aqueous and solid phases.

DNAPL Phase Distribution - Four Phase System

It is apparent from Figures 1 and 2 that the DNAPL may be present in the subsurface in various physical states or what is referred to as phases. As illustrated in Figure 3, there are four possible phases: gaseous, solid, water, and immiscible hydrocarbon (DNAPL) in the unsaturated zone. Contaminants associated with the release of DNAPL can, therefore, occur in four phases described as follows:

1. Air phase - contaminants may be present as vapors;
2. Solid phase - contaminants may adsorb or partition onto the soil or aquifer material;
3. Water phase - contaminants may dissolve into the water according to their solubility; and
4. Immiscible phase - contaminants may be present as dense nonaqueous phase liquids.

The four phase system is the most complex scenario because there are four phases and the contaminant can partition between any one or all four of these phases, as illustrated in Figure 4. For example, TCE introduced into the subsurface as a DNAPL may partition onto the soil phase, volatilize into the soil gas, and solubilize into the water phase resulting in contamination in all four phases. TCE can also partition between the water and soil, water and air, and between the soil and air. There are six pathways of phase distribution in the unsaturated zone. The distribution of a contaminant between these phases can be represented by empirical relationships referred to as partition coefficients. The partition coefficients, or the distribution of the DNAPL between the four phases, is highly site-specific and highly dependent on the characteristics of both the soil/aquifer matrix and the DNAPL. Therefore, the distribution between phases may change with time and/or location at the same site and during different stages of site remediation.

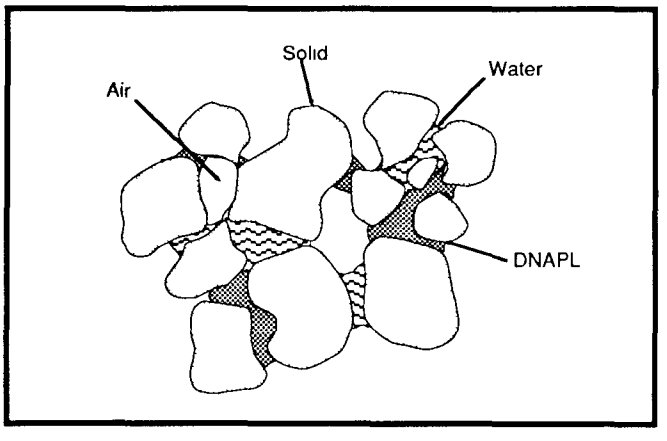

Figure 3. A DNAPL contaminated unsaturated zone has four physical states or phases (air, solid, water, immiscible). The contaminant may be present in any one, or all four phases.

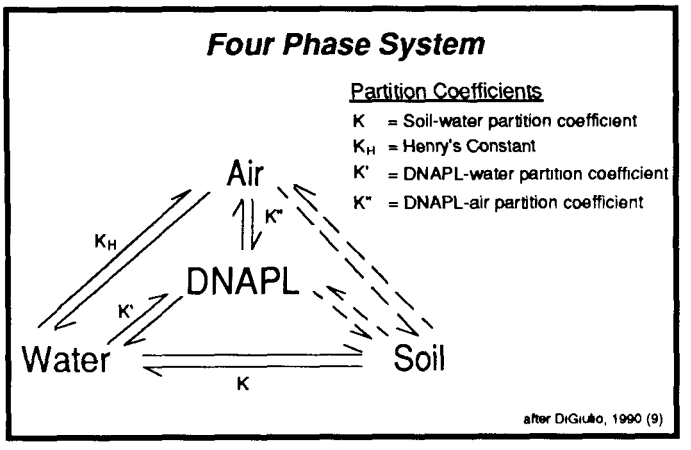

Figure 4. Distribution of DNAPL between the four phases found in the vadose zone.

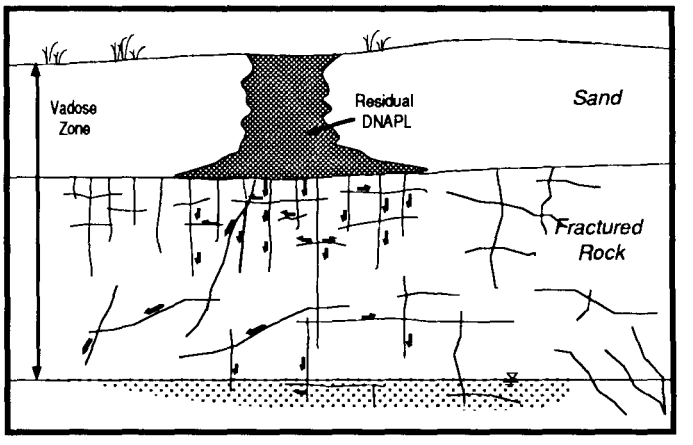

Figure 5. DNAPL spilled into fractured rock systems may follow a complex distribution of the preferential pathways.

The concept of phase distribution is critical in decision-making. Understanding the phase distribution of a DNAPL introduced into the subsurface provides significant insight in determining which tools are viable options with respect to site characterization and remediation.

DNAPL represented by residual saturation in the four phase diagram is largely immobile under the usual subsurface pressure conditions and can migrate further only: 1) in water according to its solubility; or 2) in the gas phase of the unsaturated zone (47). DNAPL components adsorbed onto the soil are also considered immobile. The mobile phases are, therefore, the soluble and volatile components of the DNAPL in the water and air, respectively.

The pore space in the unsaturated zone may be filled with one or all three fluid phases (gaseous, aqueous, immiscible). The presence of DNAPL as a continuous immiscible phase has the potential to be mobile. The mobility of DNAPL in the subsurface must be evaluated on a case by case basis. The maximum number of potentially mobile fluid phases is three. Simultaneous flow of the three phases (air, water, and immiscible) is considerably more complicated than two-phase flow (46). The mobility of three phase flow in a four-phase system is complex, poorly understood, and is beyond the scope of this DNAPL overview. The relative mobility of the two phases, water and DNAPL, in a three-phase system is presented below in the section entitled "Relative Permeability."

Generally, rock aquifers contain a myriad of cracks (fractures) of various lengths, widths, and apertures (32). Fractured rock systems have been described as rock blocks bounded by discrete discontinuities comprised of fractures, joints, and shear zones which may be open, mineral-filled, deformed, or any combination thereof (61). The unsaturated zone overlying these fractured rock systems also contain the myriad of preferential pathways. DNAPL introduced into such formations (Figure 5) follow complex pathways due to the heterogeneous distribution of the cracks, conduits, and fractures', i.e., preferential pathways. Transport of DNAPL may follow non-Darcian flow in the open fractures and/or Darcian flow in the porous media filled fractures. Relatively small volumes of NAPL may move deep, quickly into the rock because the retention capacity offered by the dead-end fractures and the immobile fragments and globules in the larger fractures is so small (32). Currently, the capability to collect the detailed information for a complete description of a contaminated fractured rock system is regarded as neither technically possible nor economically feasible (61).

Low permeability stratigraphic units such as high clay content formations may also contain a heterogeneous distribution of preferential pathways. As illustrated in Figure 6, DNAPL transport in these preferential pathways is correspondingly complex. Typically, it is assumed that high clay content formations are impervious to DNAPL. However, as DNAPL spreads out on low permeable formations it tends to seek out zones of higher permeability. As a result, preferential pathways allow the DNAPL to migrate further into the low permeable formation, or through it to underlying stratigraphic units. It is apparent from Figures 5 and 6 that the complexity of DNAPL transport may be significant prior to reaching the water table.

Saturated Zone

The second general scenario is one in which the volume of DNAPL is sufficient to overcome the fraction depleted by the residual saturation in the vadose zone, as illustrated in Figure 7. Consequently, the DNAPL reaches the water table and contaminates the ground water directly. The specific gravity of DNAPL is greater than water, therefore, the DNAPL migrates into the saturated zone. In this scenario, DNAPL continues the vertical migration through the saturated zone until the volume is eventually exhausted by the residual saturation process or until it is intercepted by a low permeable formation where it begins to migrate laterally.

DNAPL Phase Distribution - Three Phase System

Due to the lack of the gaseous phase, the saturated zone containing DNAPL is considered a three-phase system consisting of the solid, water, and immiscible hydrocarbon (Figure 8). Contaminant distribution in the three-phase system is less complex than the four-phase system. Again, this is highly dependent on the characteristics of both the aquifer

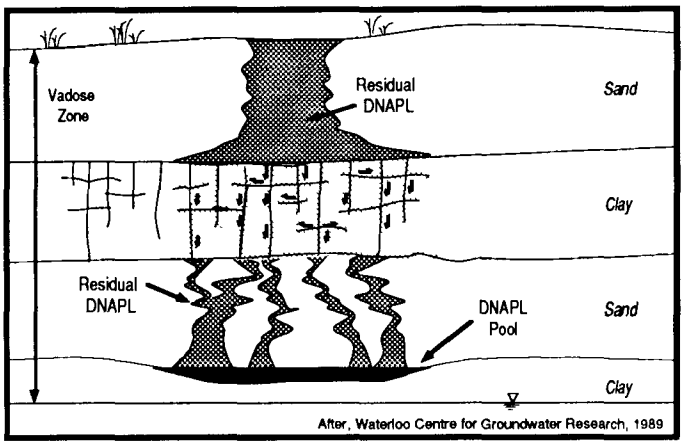

Figure 6. DNAPL spilled into a low permeable formation may follow a complex distribution of preferential pathways. The volume of DNAPL is exhausted in the vadose zone prior to reaching the water table.

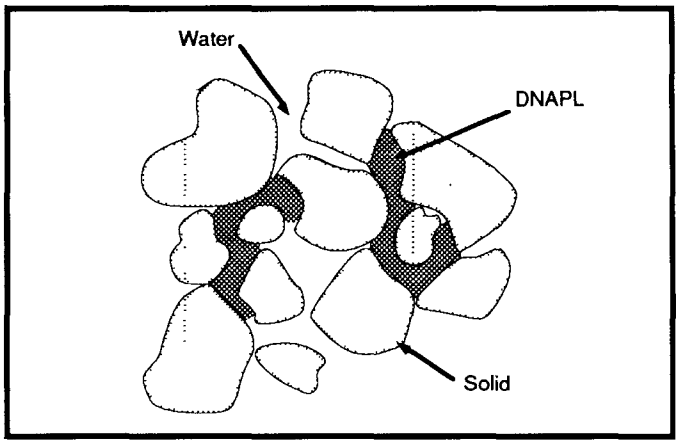

Figure 8. A DNAPL contaminated saturated zone has three phases (solid, water, immiscible). The contaminant may be present in any one, or all three phases.

matrix and the DNAPL. Figure 9 indicates the three phases and the transfer of the mass of contaminant between the phases. In this scenario, there are only three pathways of phase distribution in the saturated zone.

Note that when the DNAPL is represented by residual saturation in the three-phase system, the mobile phase of the contaminant is the water soluble components of the DNAPL and the immobile phases are the residual saturation and the adsorbed components of the DNAPL associated with the aquifer material. The main mobilization mechanism of the residual saturation is removal of soluble phase components into the ground water. When the DNAPL is present as a continuous immiscible phase, it too is considered one of the mobile phases of the contaminant. While the continuous phase DNAPL has the potential to be mobile, immobile continuous phase DNAPL may also exist in the subsurface. Although the saturated zone is considered a three-phase system, gaseous vapors from DNAPL in the unsaturated zone does have the potential to affect ground-water quality, as was indicated earlier in Figure 2.

Assuming the residual saturation in the saturated zone does not deplete the entire volume of the DNAPL, the DNAPL will continue migrating vertically until it encounters a zone or stratigraphic unit of lower permeability. Upon reaching the zone of lower permeability, the DNAPL will begin to migrate laterally. The hydraulic conductivity in the vertical direction is typically less than in the horizontal direction. It is not uncommon to find vertical conductivity that is one-fifth or one-tenth the horizontal value (4). It is expected that DNAPL spilled into the subsurface will have a significant potential to migrate laterally. If the lower permeable boundary is "bowl shaped", the DNAPL will pond as a reservoir (refer to Figure 10). As illustrated in Figure 11, it is not uncommon to observe a perched DNAPL reservoir where a discontinuous impermeable layer; i.e., silt or clay lens, intercepts the vertical migration of DNAPL. When a sufficient volume of DNAPL has been released and multiple discontinuous impermeable layers exist, the DNAPL may be present in several perched reservoirs as well as a deep

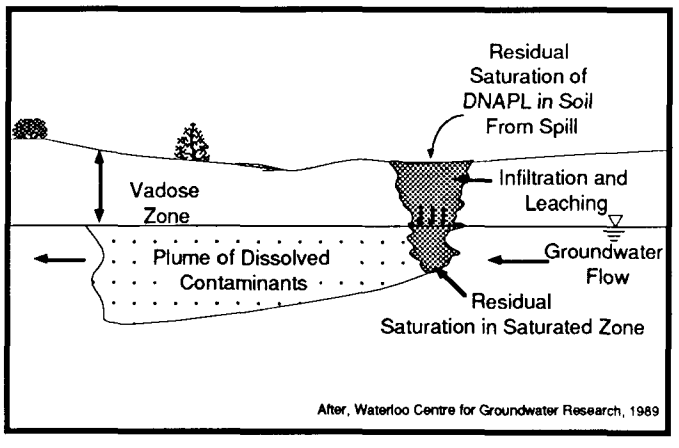

Figure 7. The volume of DNAPL is sufficient to overcome the residual saturation in the vadose zone and consequently penetrates the water table.

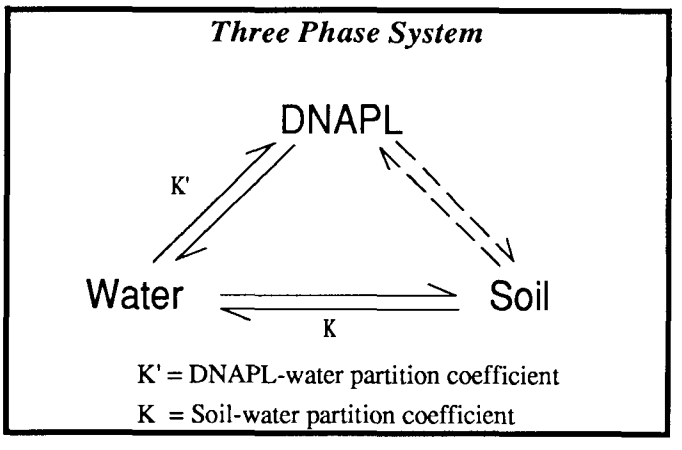

Figure 9. Distribution of DNAPL between the three phases found in the saturated zone.

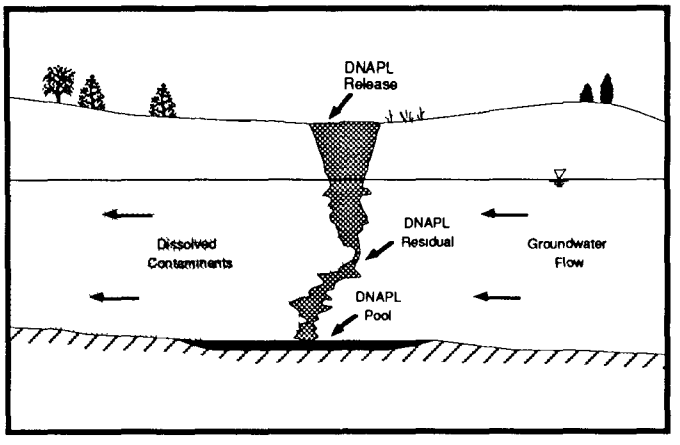

Figure 10. Migration of DNAPL through the vadose zone to an impermeable boundary.

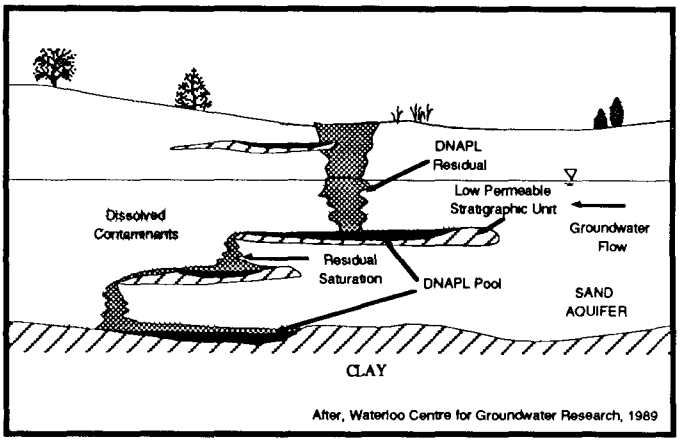

Figure 12. Perched and deep DNAPL reservoirs.

reservoir (refer to Figure 12). Lateral migration continues until either the residual saturation depletes the DNAPL or an impermeable depression immobilizes the DNAPL in a reservoir type scenario. Soluble-phase components of the DNAPL will partition into the ground water from both the residual saturation or DNAPL pools. The migration of DNAPL vertically through the aquifer results in the release of soluble-phase components of the DNAPL across the entire thickness of the aquifer. Note, that ground water becomes contaminated as it flows through, and around, the DNAPL contaminated zone.

As indicated earlier, DNAPL will migrate laterally upon reaching a stratigraphic unit of lower permeability. Transport of DNAPL will therefore be largely dependent on the gradient of the stratigraphy. Occasionally, the directional gradient of an impermeable stratigraphic unit may be different than the direction of ground-water flow as illustrated in Figure 13a. This may result in the migration of the continuous phase DNAPL in a direction different from the ground-water flow. Nonhorizontal stratigraphic units with varying hydraulic conductivity may also convey DNAPL in a different direction than ground-water flow, and at different rates (refer to Figure 13b). Determination of the direction of impermeable stratigraphic units will therefore provide useful information concerning the direction of DNAPL transport.

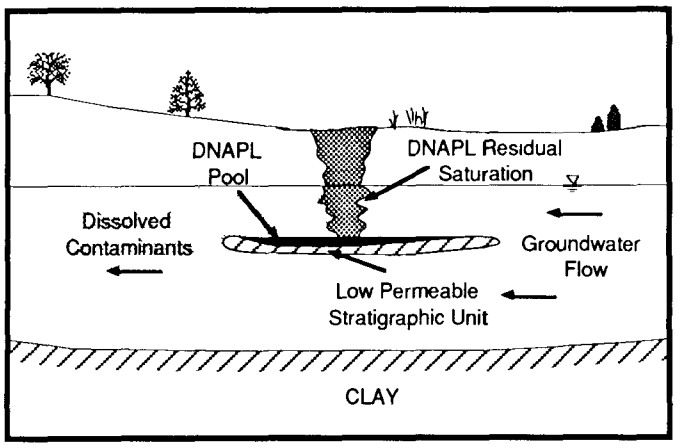

Figure 11. Perched DNAPL reservoir.

Similar to the unsaturated zone, the saturated zone also contains a complex distribution of preferential pathways from cracks, fractures, joints, etc. DNAPL introduced into such formations correspondingly follow the complex network of pathways through an otherwise relatively impermeable rock material. Other pathways which may behave as vertical conduits for DNAPL include root holes, stratigraphic windows, disposal wells, unsealed geotechnical boreholes, improperly sealed hydrogeological investigation sampling holes and monitoring wells, and old uncased/unsealed water supply wells (72). Transport of the DNAPL may migrate very rapidly in these open conduits or follow Darcian flow in the surrounding porous media or porous media filled fractures. A relatively small volume of DNAPL can move deep into a fractured system due to the low retentive capacity of the fractured system. Consequently, fractured clay or rock stratigraphic units, which are often considered lower DNAPL boundary conditions, may have preferential pathways leading to lower formations, as depicted in Figure 14. Careful inspection of soil cores at one Superfund site indicated that DNAPL flow mainly occurred through preferential pathways and was not uniformly distributed throughout the soil mass (8). Due to the complex

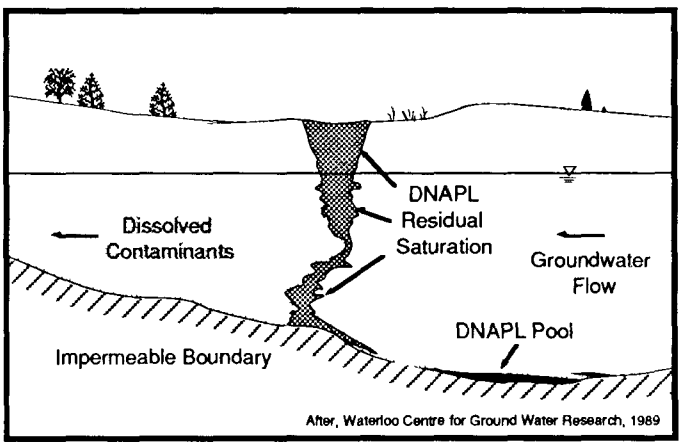

Figure 13a. Stratigraphic gradient different from ground water gradient results in a different direction of flow of the ground water and continuous phase DNAPL.

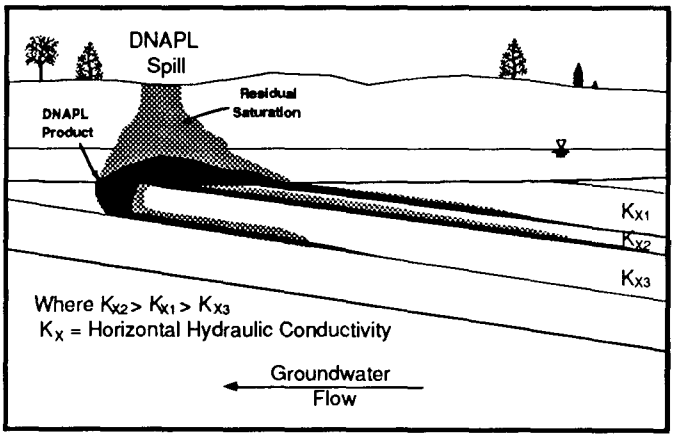

Figure 13b. Non-horizontal stratigraphic units with variable hydraulic conductivity may convey DNAPL in a different direction than the ground water flow direction.

distribution of preferential pathways, characterization of the volume distribution of the DNAPL is difficult.

Important DNAPL Transport and Fate Parameters

There are several characteristics associated with both the subsurface media and the DNAPL which largely determine the fate and transport of the DNAPL. A brief discussion of these parameters is included to help identify the specific details of DNAPL transport mechanisms. Several of the distinctive DNAPL phenomena observed on the field-scale relates back to phenomena at the pore-scale. Therefore, it is important to understand the principles from the pore-scale level to develop an understanding of field-scale observations, which is the scale at which much of the Superfund work occurs. A more complete and comprehensive review of these parameters is available (2,36,71).

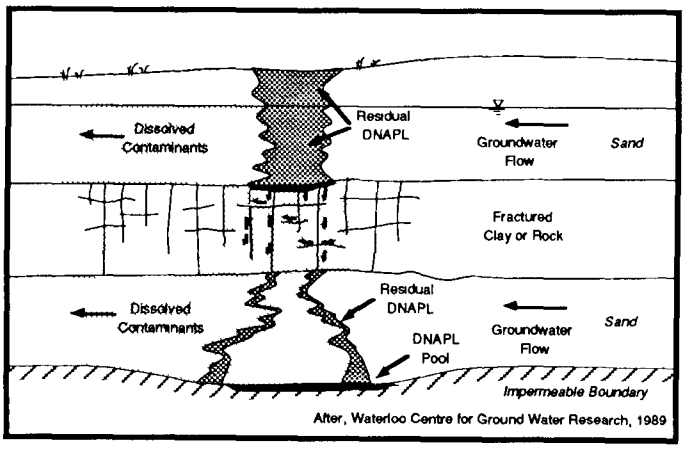

Figure 14. DNAPL transport in fracture and porous media stratigraphic units.

DNAPL Characteristics

Density

Fluid density is defined as the mass of fluid per unit volume, i.e. g/cm^3. Density of an immiscible hydrocarbon fluid is the parameter which delineates LNAPL's from DNAPL's. The property varies not only with molecular weight but also molecular interaction and structure. In general, the density varies with temperature and pressure (2). Equivalent methods of expressing density are specific weight and specific gravity. The specific weight is defined as the weight of fluid per unit volume, i.e. lb/ft^3. The specific gravity (S.G.) or the relative density of a fluid is defined as the ratio of the weight of a given volume of substance at a specified temperature to the weight of the same volume of water at a given temperature (31). The S.G. is a relative indicator which ultimately determines whether the fluid will float (S.G.< 1.0) on, or penetrate into (S.G.>1.0) the water table. Table 1 contains a list of compounds with a density greater than one that are considered DNAPL's. Note, however, that while the specific gravity of pentachlorophenol and the non-halogenated semi-volatiles is greater than 1.00, these compounds are a solid at room temperature and would not be expected to be found as an immiscible phase liquid at wood preserving sites but are commonly found as contaminants. Pentachlorophenol is commonly used as a wood preservant and is typically dissolved (4-7%) in No. 2 or 3 fuel oil.

Viscosity

The viscosity of a fluid is a measure of its resistance to flow. Molecular cohesion is the main cause of viscosity. As the temperature increases in a liquid, the cohesive forces decrease and the absolute viscosity decreases. The lower the viscosity, the more readily a fluid will penetrate a porous media. The hydraulic conductivity of porous media is a function of both the density and viscosity of the fluid as indicated in equation [1]. It is apparent from this equation that fluids with either a viscosity less than water or fluids with a density greater than water have the potential to be more mobile in the subsurface, than water.

$$K = \frac{k \rho g}{\mu} \quad \text{where,} \quad \begin{array}{l} K = \text{hydraulic conductivity} \\ k = \text{intrinsic permeability} \\ \rho = \text{fluid mass density} \\ g = \text{gravity} \\ \mu = \text{dynamic (absolute) viscosity} \end{array} \qquad [1]$$

Results from laboratory experiments indicated that several chlorinated hydrocarbons which have low viscosity (methylene chloride, perchloroethylene, 1,1,1-TCA, TCE) will infiltrate into soil notably faster than will water (47). The relative value of NAPL viscosity and density, to water, indicates how fast it will flow in porous media (100% saturated) with respect to water. For example, several low viscosity chlorinated hydrocarbons (TCE, tetrachloroethylene, 1,1,1-TCA, Methylene Chloride, Chloroform, Carbon Tetrachloride, refer to Table 1) will flow 1.5-3.0 times as fast as water and higher viscosity compounds including light heating oil, diesel fuel, jet fuel, and crude oil (i.e. LNAPL's) will flow 2-10 times slower than water (45). Both coal tar and creosote typically have a specific gravity greater than one and a viscosity greater than water. It is interesting to note

that the viscosity of NAPL may change with time (36). As fresh crude oils lose the lighter volatile components from evaporation, the oils become more viscous as the heavier components compose a larger fraction of the oily mixture resulting in an increase in viscosity.

Solubility

When an organic chemical is in physical contact with water, the organic chemical will partition into the aqueous phase. The equilibrium concentration of the organic chemical in the aqueous phase is referred to as its solubility. Table 1 presents the solubility of several of the most commonly found DNAPL's at EPA Superfund Sites. The solubility of organic compounds varies considerably from the infinitely miscible compounds, including alcohols (ethanol, methanol) to extremely low solubility compounds such as polynuclear aromatic compounds.

Numerous variables influence the solubility of organic compounds. The pH may affect the solubility of some organic compounds. Organic acids may be expected to increase in solubility with increasing pH, while organic bases may act in the opposite way (31). For example, pentachlorophenol is an acid which is ionized at higher pH's. In the ionized form, pentachlorophenol would be more soluble in water (59). Solubility in water is a function of the temperature, but the strength and direction of this function varies. The presence of dissolved salts or minerals in water leads to moderate decreases in solubility (31). In a mixed solvent system, consisting of water and one or more water-miscible compounds, as the fraction of the cosolvent in the mixture increases, the solubility of the organic chemical increases exponentially (12). In general, the greater the molecular weight and structural complexity of the organic compound, the lower the solubility.

Organic compounds are only rarely found in ground water at concentrations approaching their solubility limits, even when organic liquid phases are known or suspected to be present. The observed concentrations are usually more than a factor of 10 lower than the solubility presumably due to diffusional limitations of dissolution and the dilution of the dissolved organic contaminants by dispersion (74). This has also been attributed to: reduced solubility due to the presence of other soluble compounds, the heterogeneous distribution of DNAPL in the subsurface, and dilution from monitoring wells with long intake lengths (10). Detection of DNAPL components in the subsurface below the solubility should clearly not be interpreted as a negative indicator for the presence of DNAPL.

In a DNAPL spill scenario where the DNAPL or its vapors are in contact with the ground water, the concentration of the soluble phase components may range from non-detectable up to the solubility of the compound. The rate of dissolution has been expressed as a function of the properties of the DNAPL components (solubility), ground water flow conditions, differential between the actual and solubility concentration, and the contact area between the DNAPL and the ground water (10). The contact area is expected to be heterogeneous and difficult to quantify. Additionally, as the time of contact increases between the DNAPL and the water, the concentration in the aqueous phase increases.

Vapor Pressure

The vapor pressure is that characteristic of the organic chemical which determines how readily vapors volatilize or evaporate from the pure phase liquid. Specifically, the partial pressure exerted at the surface by these free molecules is known as the vapor pressure (30). Molecular activity in a liquid tends to free some surface molecules and this tendency towards vaporization is mainly dependent on temperature. The vapor pressure of DNAPL's can actually be greater than the vapor pressure of volatile organic compounds. For example, at 20 C, the ratio of the vapor pressures of TCE and benzene is 1.4 (1).

Volatility

The volatility of a compound is a measure of the transfer of the compound from the aqueous phase to the gaseous phase. The transfer process from the water to the atmosphere is dependent on the chemical and physical properties of the compound, the presence of other compounds, and the physical properties (velocity, turbulence, depth) of the water body and atmosphere above it. The factors that control volatilization are the solubility, molecular weight, vapor pressure, and the nature of the air-water interface through which it must pass (31). The Henry's constant is a valuable parameter which can be used to help evaluate the propensity of an organic compound to volatilize from the water. The Henry's law constant is defined as the vapor pressure divided by the aqueous solubility. Therefore, the greater the Henry's law constant, the greater the tendency to volatilize from the aqueous phase, refer to Table 1.

Interfacial Tension

The unique behavior of DNAPLs in porous media is largely attributed to the interfacial tension which exists between DNAPL and water, and between DNAPL and air. These interfacial tensions, result in distinct interfaces between these fluids at the pore-scale. When two immiscible liquids are in contact, there is an interfacial energy which exists between the fluids resulting in a physical interface. The interfacial energy arises from the difference between the inward attraction of the molecules in the interior of each phase and those at the surface of contact (2). The greater the interfacial tension between two immiscible liquids; the less likely emulsions will form; emulsions will be more stable if formed, and the better the phase separation after mixing. The magnitude of the interfacial tension is less than the larger of the surface tension values for the pure liquids, because the mutual attraction of unlike molecules at the interface reduces the large imbalance of forces (31). Interfacial tension decreases with increasing temperature, and may be affected by pH, surfactants, and gases in solution (36). When this force is encountered between a liquid and a gaseous phase, the same force is called the surface tension (66).

The displacement of water by DNAPL and the displacement of DNAPL by water in porous media often involves a phenomena referred to as immiscible fingering. The lower the interfacial tension between immiscible fluids, the greater the instability of the water:DNAPL interface and thus the greater the immiscible fingering (27). The distribution of the fingering effects in porous media has been reported to be a function of the density, viscosity, surface tension (27) and the displacement velocity

(13) of the fluids involved as well as the porous media heterogeneity (28).

Wettability

Wettability refers to the relative affinity of the soil for the various fluids - water, air, and the organic phase. On a solid surface, exposed to two different fluids, the wettability can be inferred from the contact angle (66), also referred to as the wetting angle, refer to Figure 15. In general, if the wetting angle is less than 90 degrees, the fluid is said to be the wetting fluid. In this scenario, water will preferentially occupy the smaller pores and will be found on solid surfaces (14). When the wetting angle is near 90 degrees, neither fluid is preferentially attracted to the solid surfaces. If the wetting angle is greater than 90 degrees, the DNAPL is said to be the wetting fluid. The wetting angle is an indicator used to determine whether the porous material will be preferentially wetted by either the hydrocarbon or the aqueous phase (71). Wettability, therefore, describes the preferential spreading of one fluid over solid surfaces in a two-fluid system. The wetting angle, which is a measure of wettability, is a solid-liquid interaction and can actually be defined in terms of interfacial tensions (71). Several methods have been developed to measure the wetting angle (36,71). In most natural systems, water is the wetting fluid, and the immiscible fluid is the non-wetting fluid. Coal tar may be the exception (i.e. contact angle greater than 90 degrees), which is mainly attributed to the presence of surfactants (70). The wetting fluid will tend to coat the surface of grains and occupy smaller spaces (i.e. pore throats) in porous media, the non-wetting fluid will tend to be restricted to the largest openings (47).

The wetting angle depends on the character of the solid surface on which the test is conducted. The test is conducted on flat plates composed of minerals which are believed representative of the media, or on glass. Contact angle measurements for crude oil indicates that the wetting angles vary widely depending on the mineral surface (53). Soil and aquifer material are not composed of homogeneous mineral composition nor flat surfaces. The measured wetting angle can only be viewed as a qualitative indicator of wetting behavior.

The reader is recommended to refer to reference No. 31 for review of the basic principles and for various techniques to measure the following DNAPL parameters: density, viscosity, interfacial tension, solubility, vapor pressure, and volatility.

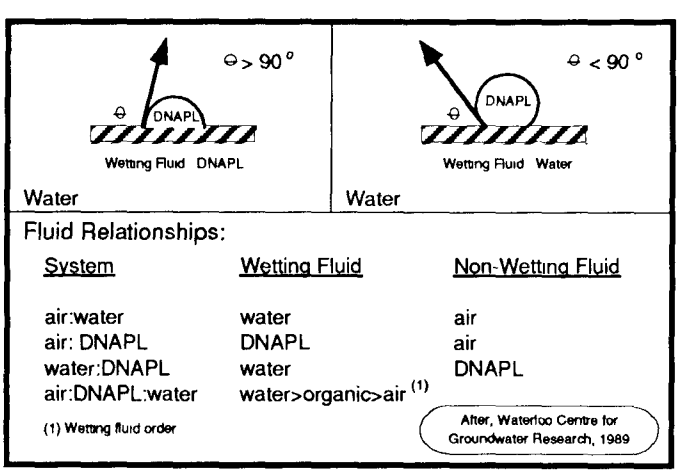

Figure 15. Wetting angle and typical wetting fluid relationships.

Subsurface Media Characteristics

Capillary Force/Pressure

Capillary pressure is important in DNAPL transport because it largely determines the magnitude of the residual saturation that is left behind after a spill incident. The greater the capillary pressure, the greater the potential for residual saturation. In general, the capillary force increases in the following order; sand, silt, clay. Correspondingly, the residual saturation increases in the same order. Capillary pressure is a measure of the tendency of a porous medium to suck in the wetting fluid phase or to repel the nonwetting phase (2). Capillary forces are closely related to the wettability of the porous media. The preferential attraction of the wetting fluid to the solid surfaces cause that fluid to be drawn into the porous media. Capillary forces are due to both adhesion forces (the attractive force of liquid for the solids on the walls of the channels through which it moves) and cohesion forces (the attraction forces between the molecules of the liquid) (32). The capillary pressure depends on the geometry of the void space, the nature of solids and liquids, the degree of saturation (2) and in general, in-creases with a decrease in the wetting angle and in pore size, and with an increase in the interfacial tension (71). All pores have some value of capillary pressure. Before a nonwetting fluid can enter porous media, the capillary pressure of the largest pores (smallest capillary pressure) must be exceeded. This minimum capillary pressure is called the entry pressure.

In the unsaturated zone, pore space may be occupied by water, air (vapors), or immiscible hydrocarbon. In this scenario, capillary pressure retains the water (wetting phase) mainly in the smaller pores where the capillary pressure is greatest. This restricts the migration of the DNAPL (non-wetting phase) through the larger pores unoccupied by water. Typically, DNAPL does not displace the pore water from the smaller pores. It is interesting to note that the migration of DNAPL through fine material (high capillary pressure) will be impeded upon reaching coarser material (low capillary pressure).

The capillary fringe will obstruct the entry of the DNAPL into the saturated zone. When a sufficient volume of DNAPL has been released and the "DNAPL pressure head" exceeds the water capillary pressure at the capillary fringe (entry pressure), the DNAPL will penetrate the water table. This is why DNAPL is sometimes observed to temporarily flatten out on top of the water table. Similarly, laboratory experiments have been conducted in which DNAPL (tetrachloroethylene) infiltrating through porous media was found to flow laterally and cascade off lenses too fine to penetrate (28), (refer to Figure 11). This was attributed to the inability of the DNAPL to overcome the high capillary pressure associated with the lenses. Logically, when "DNAPL pressure head" exceeds the capillary pressure, the DNAPL will penetrate into the smaller pores. These laboratory experiments are important because they illustrate that small differences in the capillary characteristics of porous media can induce significant lateral flow of non-wetting fluids.

A comprehensive investigation of capillary trapping and multiphase flow of organic liquids in unconsolidated porous media revealed many intricacies of this process in the vadose and saturated zone (66). An important note is that while capillary pressure is rarely measured at hazardous waste sites,

the soil texture (sand, silt, clay) is usually recorded during drilling operations and soil surveys. This information, along with soil core analyses will help to delineate the stratigraphy and the volume distribution of NAPL.

Pore Size Distribution/Initial Moisture Content

In natural porous media, the geometry of the pore space is extremely irregular and complex (2). The heterogeneity of the subsurface environment i.e. the variability of the pore size distribution, directly affects the distribution of the capillary pressures along the interfaces between the aqueous and immiscible phases (50). In saturated column experiments, it was observed that NAPL preferentially traveled through strings of macropores, almost completely by-passing the water filled micropores (66). In the same study, a heterogeneous distribution of coarse and fine porous material was simulated. Most of the incoming organic liquid preferentially traveled through the coarse lens material.

In short term column drainage experiments, results indicated that the particle grain size is of primary importance in controlling the residual saturation of a gasoline hydrocarbon (19). Fine and coarse sands (dry) were found to have 55% and 14% residual saturation, respectively. The finer the sand, the greater the residual saturation. During these experiments, the residual saturation was reduced 20-30% in a medium sand and 60% in a fine sand when the sands were initially wet. Soil pore water held tightly by capillary forces in the small pores will limit the NAPL to the larger pores, and thus, result in lower residual saturation. In a similar laboratory (unsaturated) column study, the smaller the grain size used in the experiment, the greater the residual saturation of the NAPL (74). The residual saturation in the saturated column experiments was found to be greater than the unsaturated columns and was independent of the particle size distribution.

These observations follow traditional capillary force theory. Residual saturation resulting from a DNAPL spill in the unsaturated zone is highly dependent on the antecedent moisture content in the porous media. When the moisture content is low, the strong capillary forces in the smaller pores will tenaciously draw in and hold the DNAPL. When the moisture content is high, the capillary forces in the smaller pores will retain the soil pore water, and DNAPL residual saturation will mainly occur in the larger pores. Therefore, greater residual saturation can be expected in dryer soils. Correspondingly, NAPL will migrate further in a wetter soil, and displacement of NAPL from small pores is expected to be more difficult than from large pores.

Stratigraphic Gradient

DNAPL migrating vertically will likely encounter a zone or stratigraphic unit of lower vertical permeability. A reduction in the vertical permeability of the porous media will induce lateral flow of the DNAPL. The gradient of the lower permeable stratigraphic unit will largely determine the direction in which the DNAPL will flow. This is applicable to both the saturated and unsaturated zones. As depicted in Figures 13a and 13b, the lateral direction of DNAPL flow may be in a different direction than ground-water flow.

Ground Water Flow Velocity

The ground water flow velocity is a dynamic stress parameter which tends to mobilize the hydrocarbon (39). As the ground water velocity increases, the dynamic pressure and viscous forces increase. Mobilization of DNAPL occurs when the viscous forces of the ground water acting on the DNAPL, exceeds the porous media capillary forces retaining the DNAPL.

Saturation Dependent Functions

Residual Saturation

Residual saturation is defined as the volume of hydrocarbon trapped in the pores relative to the total volume of pores (38) and therefore is measured as such (74). Residual saturation has also been described as the saturation at which NAPL becomes discontinuous and is immobilized by capillary forces (36). The values of residual saturation vary from as low as 0.75 - 1.25% for light oil in highly permeable media to as much as 20% for heavy oil (50). Residual saturation values have also been reported to range from 10% to 50% of the total pore space (39,74). Other researchers reported that residual saturation values appear to be relatively insensitive to fluid properties and very sensitive to soil properties (and heterogeneities) (66). Laboratory studies conducted to predict the residual saturation in soils with similar texture and grain size distribution yielded significantly different values. It was concluded that minor amounts of clay or silt in a soil may play a significant role in the observed values.

In the unsaturated zone during low moisture conditions, the DNAPL residual saturation will wet the grains in a pendular state (a ring of liquid wrapped around the contact point of a pair of adjacent grains). During high moisture conditions, the wetting fluid, which is typically water, will preferentially occupy the pendular area of adjacent grains and the hydrocarbon will occupy other available pore space, possibly as isolated droplets. In the saturated zone, the DNAPL residual saturation will be present as isolated drops in the open pores (47). Furthermore, results of laboratory experimentation indicated that residual saturation increased with decreasing hydraulic conductivity in both the saturated and unsaturated zones and that the residual saturation is greatest in the saturated zone. Laboratory experiments indicated that vadose zone residual saturation was roughly one third of the residual saturation in the saturated zone (66). The increase in residual saturation in the saturated zone is due to the following: [1] the fluid density ratio (DNAPL:air versus DNAPL:water above and below the water table, respectively) favors greater drainage in the vadose zone; [2] as the non-wetting fluid in most saturated media, NAPL is trapped in the larger pores; and, [3] as the wetting fluid in the vadose zone, NAPL tends to spread into adjacent pores and leave a lower residual content behind, a process that is inhibited in the saturated zone (36). Thus, the capacity for retention of DNAPLs in the unsaturated zone is less than the saturated zone.

Relative Permeability

Relative permeability is defined as the ratio of the permeability of a fluid at a given saturation to its permeability at 100% saturation. Thus it can have a value between 0 and 1 (71).

Figure 16 illustrates a relative permeability graph for a two fluid phase system showing the relationship between the observed permeability of each fluid for various saturations to that of the observed permeability if the sample were 100% saturated with that fluid (73). The three regions of this graph are explained as follows (71): Region I has a high saturation of DNAPL and is considered a continuous phase while the water is a discontinuous phase, therefore, water permeability is low. Assuming the DNAPL is the non-wetting fluid, water would fill the smaller capillaries and flow through small irregular pores. In Region II, both water and DNAPL are continuous phases although not necessarily in the same pores. Both water and

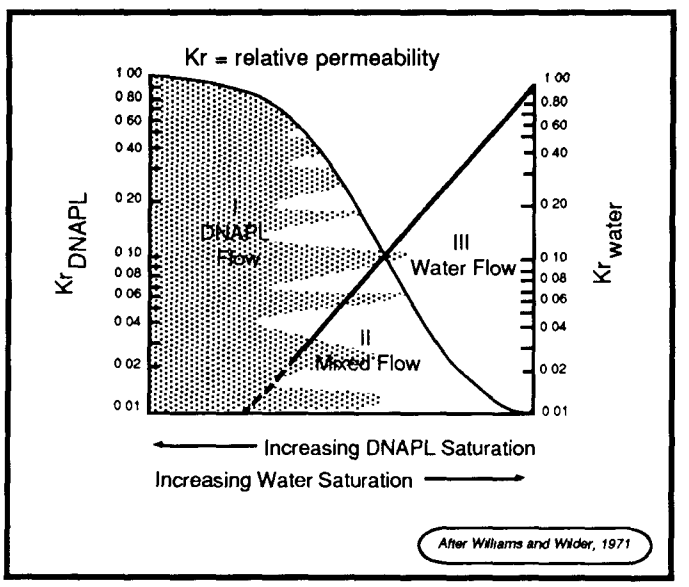

Figure 16. Relative permeability graph.

NAPL flow simultaneously. However, as saturation of either phase increases, the relative permeability of the other phase correspondingly decreases. Region III exhibits a high saturation of water while the DNAPL phase is mainly discontinuous. Water flow dominates this region and there is little or no flow of DNAPL.

Both fluids flow through only a part of the pore space and thus only a part of the cross section under consideration is available for flow of each fluid. Therefore, the discharge of each fluid must be lower corresponding to its proportion of the cross sectional area (46).

Figure 17 is another relative permeability graph which demonstrates several points. Small increases in DNAPL saturation results in a significant reduction in the relative permeability of water. However, a small increase in water saturation does not result in a significant reduction in DNAPL relative permeability. This figure identifies two points, SO1 and SO2, where the saturation of the DNAPL and the water are greater than 0 before there is a relative permeability for this fluid. The two fluids hinder the movement of the other to different degrees and both must reach a minimum saturation before they achieve any mobility at all (47). These minimum saturations, for the water and DNAPL, are identified as irreducible and residual saturation, respectively.

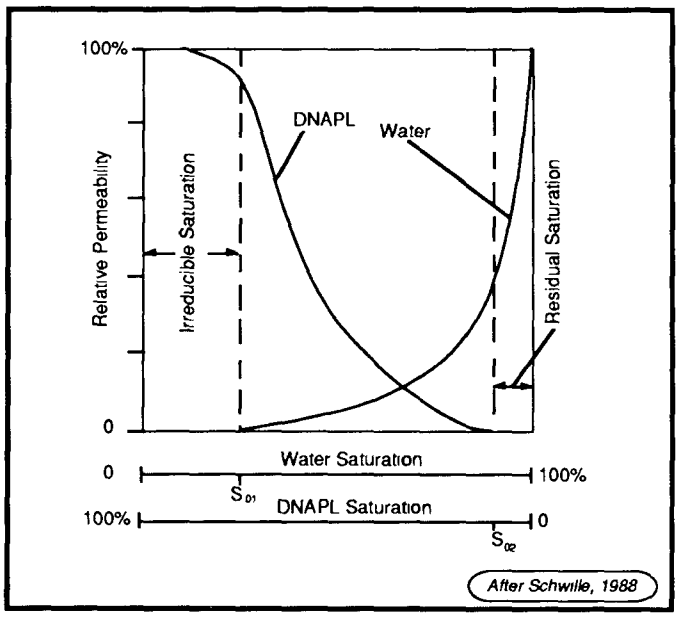

Figure 17. The relative permeability curves for water and a DNAPL in a porous medium as a function of the pore space saturation.

Site Characterization for DNAPL

Characterization of the subsurface environment at hazardous waste sites containing DNAPL is complex and will likely be expensive. Specific details associated with the volume and timing of the DNAPL release are usually poor or are not available and subsurface heterogeneity is responsible for the complicated and unpredictable migration pathway of subsurface DNAPL transport. As discussed previously, slight changes in vertical permeability may induce a significant horizontal component to DNAPL migration.

Site characterization typically involves a significant investment in ground-water analyses. Although analysis of ground water provides useful information on the distribution of the soluble components of the DNAPL, the presence of other phases of the DNAPL may go unrecognized. The investigation must, therefore, be more detailed to obtain information concerning the phase distribution of the DNAPL at a site. Site characterization may require analyses on all four phases (aqueous, gaseous, solid, immiscible) to yield the appropriate information (refer to Table 2). In brief, data collected on the various phases must be compiled, evaluated and used to help identify: where the contaminant is presently located; where it has been; what phases it occurs in; and what direction the mobile phases may be going. A comprehensive review of site characterization for subsurface investigations is available (68). Development of monitoring and remediation strategies can be focused more effectively and efficiently after a clear definition of the phase distribution has been completed.

Ground Water

Ground water analyses for organic compounds, in conjunction with ground water flow direction data, has repeatedly been used to: delineate the extent of ground water contamination from DNAPL; determine the direction of plume migration; and

Table 2 - Phase Distribution of DNAPL in the Subsurface

	MATRIX	PHASE
1.	ground water	aqueous - soluble components of DNAPL
2.	soil/aquifer material	solid - adsorbed components of DNAPL on solid phase material
3.	DNAPL	immiscible - continuous phase (mobile), residual saturation (immobile)
4.	soil gas	gaseous - volatile components

to identify probable DNAPL source area(s). While this approach has been used successfully to characterize the distribution of contaminants in the subsurface, there are limitations. For example, since DNAPL and ground water may flow in different directions, as indicated in Figures 13a and 13b, ground water analyses may not necessarily identify the direction of DNAPL migration.

Ground water analyses may be useful to identify probable DNAPL source areas, but, estimating the volume of DNAPL in the subsurface is limited using this approach. Soluble phase components of DNAPL are rarely found in excess of 10% of the solubility even when organic liquids are known or suspected to be present. The concentration of soluble DNAPL components in the ground water is not only a function of the amount of DNAPL present, but also the chemical and physical characteristics of the DNAPL, the contact area and time between the ground water and DNAPL, and numerous transport and fate parameters (retardation, biodegradation, dispersion, etc.). One technique has been developed using chemical ratios in the ground water as a means of source identification and contaminant fate prediction (18).

Soil/Aquifer Material

Exploratory Borings

Physical and chemical analyses of soil and aquifer material (drill cuttings, cores) from exploratory borings will provide useful information in the delineation of the horizontal and vertical mass distribution of DNAPL. While simple visual examination for physical presence or absence of contamination might seem like a worthwhile technique, it can be deceiving and does nothing to sort out the various liquid phases and their relationship to each other (71). A quantitative approach is necessary to determine DNAPL distribution.

Drill cuttings or core material brought to the surface from exploratory borings can be screened initially to help delineate the depth at which volatile components from the various phases of the hydrocarbon exists. The organic vapor analyzer and the HNU are small portable instruments that can detect certain volatile compounds in the air. These methods are used to initially screen subsurface materials for volatile components of DNAPL. Identification of individual compounds and their concentrations may be confirmed by other, more precise, analyses.

Analysis of the soil or aquifer material by more accurate means, such as gas chromatography or high pressure liquid chromatography, will take longer but will provide more specific information on a larger group of organic compounds, i.e., volatile/non-volatile, and on specific compounds. This information is necessary to help fix the horizontal and vertical mass distribution of the contaminant and to help delineate the phase distribution. These analyses do not distinguish between soluble, sorbed or free-phase hydrocarbon, however; a low relative concentration indicates that the contaminant may mainly be present in the gaseous or aqueous phases; and a high relative concentration indicates the presence of sorbed contaminant or free phase liquid either as continuous-phase or residual saturation. A more rigorous set of analyses is required to distinguish between the various phases.

Additional tests to identify the presence of NAPL in soil or aquifer core sample are currently undeveloped and research in this area is warranted. Squeezing and immiscible displacement techniques have been used to obtain the pore water from cores (40). Other methods of phase separation involving vacuum or centrifugation may also be developed for this use. A paint filter test was proposed in one Superfund DNAPL field investigation where aquifer cores were placed in a filter/funnel apparatus, water was added, and the filtrate was examined for separate phases. These core analysis techniques have potential to provide valuable field data to characterize NAPL distribution.

Cone Penetrometer

The cone penetrometer (ASTM D3441-86)(69) has been used for some time to supply data on the engineering properties of soils. Recently, the application of this technology has made the leap to the hazardous waste arena. The resistance of the formation is measured by the cone penetrometer as it is driven vertically into the subsurface. The resistance is interpreted as a measure of pore pressure, and thus provides information on the relative stratigraphic nature of the subsurface. Petroleum and chlorinated hydrocarbon plumes can be detected most effectively when the cone penetrometer is used in conjunction with in-situ sensing technologies (48). Features of the cone penetrometer include: a continuous reading of the stratigraphy/ permeability; in-situ measurement; immediate results are available; time requirements are minimal; vertical accuracy of stratigraphic composition is high; ground-water samples can be collected in-situ; and the cost is relatively low.

Data from the cone penetrometer can be used to delineate probable pathways of DNAPL transport. This is accomplished by identifying permeability profiles in the subsurface. A zone of low permeability underlying a more permeable stratigraphic unit will likely impede vertical transport of the DNAPL. Where such a scenario is found, a collection of DNAPL is probable and further steps can be implemented to more accurately and economically investigate and confirm such an occurrence. This general approach has successfully been implemented at one Superfund site (8).

DNAPL

Well Level Measurements

In an effort to delineate the horizontal and vertical extent of the DNAPL at a spill site, it is important to determine the elevation

of DNAPL in the subsurface. Monitoring DNAPL elevation over time will indicate the mobility of the DNAPL. There are several methods that can be used to determine the presence of DNAPL in a monitoring well. One method relies on the difference in electrical conductivity between the DNAPL and water. A conductivity or resistivity sensor is lowered into the well and a profile is measured. The interface of the DNAPL is accurately determined when the difference in conductivity is detected between the two fluids. This instrument may also be used to delineate LNAPL. A transparent, bottom-loading bailer can also be used to measure the thickness (and to sample) of DNAPL in a well (36). The transparent bailer is raised to the surface and the thickness of the DNAPL is made by visual measurement.

Several laboratory and field studies have been performed which investigate the anomaly between the actual and measured LNAPL levels in ground-water wells (15,16,24,25). The anomaly between actual and measured NAPL thickness in the subsurface is also applicable to DNAPL, but for different reasons. The location of the screening interval is the key to understanding both scenarios. First, if the well screen interval is situated entirely in the DNAPL layer, and the hydrostatic head (water) in the well is reduced by pumping or bailing, then to maintain hydrostatic equilibrium, the DNAPL will rise in the well (36,44,71) (refer to Figure 18). Secondly, if the well screen extends into the barrier layer, the DNAPL measured thickness will exceed that in the formation by the length of the well below the barrier surface (36) (refer to Figure 19). Both of these scenarios will result in a greater DNAPL thickness in the well and thus a false indication (overestimate) of the actual DNAPL thickness will result. One of the main purposes of the monitoring well in a DNAPL investigation is to provide information on the thickness of the DNAPL in the aquifer. Therefore, construction of the well screen should intercept the ground water:DNAPL interface and the lower end of the screen should be placed as close as possible to the impermeable stratigraphic unit.

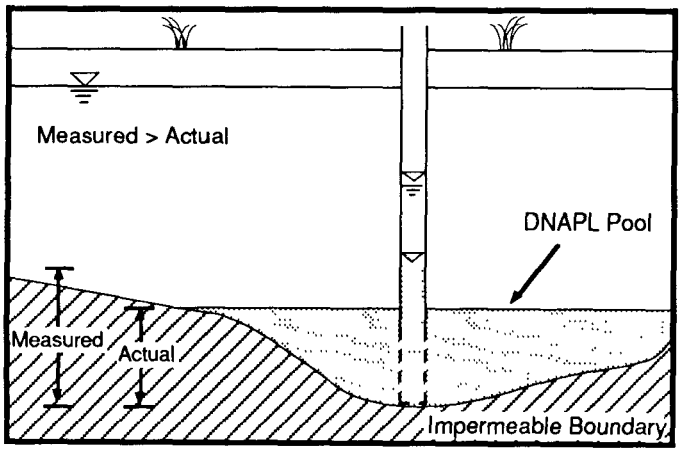

Figure 18. A well screened only in the DNAPL in conjunction with lower hydrostatic head (i.e. water) in the well may result in an overestimation of DNAPL thickness.

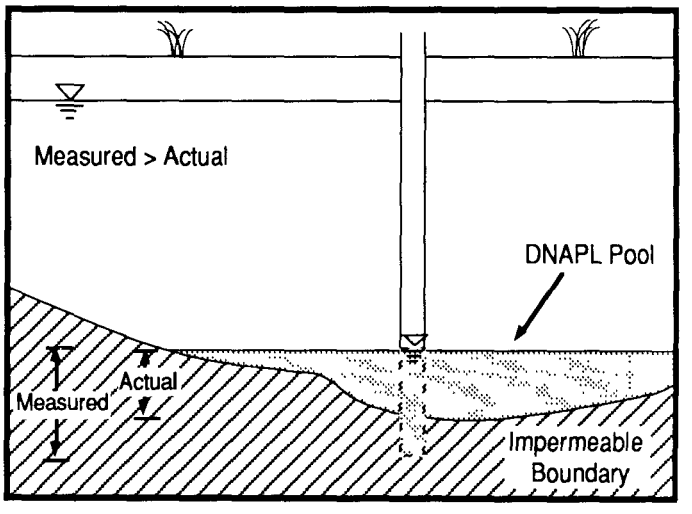

Figure 19. A well screened into an impermeable boundary may result in an over-estimation of the DNAPL thickness.

DNAPL Sampling

Sampling of DNAPL from a well is necessary to perform chemical and physical analyses on the sample. Two of the most common methods used to retrieve a DNAPL sample from a monitoring well are the peristaltic pump and the bailer. A peristaltic pump can be used to collect a sample if the DNAPL is not beyond the effective reach of the pump, which is typically less than 25 feet. The best method to sample DNAPL is to use a double check valve bailer. The key to sample collection is controlled, slow lowering (and raising) of the bailer to the bottom of the well (57). The dense phase should be collected prior to purging activities.

Soil-Gas Surveys

A soil-gas survey refers to the analysis of the soil air phase as a means to delineate underground contamination from volatile organic chemicals and several techniques have been developed (34,52). This investigative tool is mainly used as a preliminary screening procedure to delineate the areal extent of volatile organic compounds in the soil and ground water. This method is quick, less expensive than drilling wells and can provide greater plume resolution (33).

Data from a soil-gas survey is a valuable aid in the development of a more detailed subsurface investigation where ground water monitoring wells and exploratory borings are strategically located for further site characterization. There are limitations to soil-gas surveys (26,52) and data interpretation must be performed carefully (35,49). Soil-gas investigations have mainly been conducted to identify the location of the organic contaminants in ground water. At the time of this publication, the scientific literature did not contain information specifically applicable to the delineation of DNAPL from soil-gas survey data. However, it is surmisable that soil-gas surveys can be used to help delineate DNAPL residual saturation in the unsaturated zone or the location of perched DNAPL reservoirs.

Miscellaneous

The vertical migration of DNAPL in the saturated zone will eventually be challenged by a low permeability stratigraphic unit. According to the principles of capillary pressure, the lower permeability unit will exhibit a greater capillary pressure. Displacement of water by DNAPL requires that the hydrostatic force from the mounding DNAPL exceed the capillary force of the low permeability unit. The Hobson formula is used to compute the critical height calculation to overcome the capillary pressure under different pore size conditions (70).

In an effort to minimize further DNAPL contamination as a result of drilling investigations, precautionary steps should be taken. Penetration of DNAPL reservoirs in the subsurface during drilling activities offers a conduit for the DNAPL to migrate vertically into previously uncontaminated areas. It is very easy to unknowingly drill through a DNAPL pool and the bed it sits on, causing the pool to drain down the hole into a deeper part of the aquifer or into a different aquifer (32). Special attention to grouting and sealing details during and after drilling operations will help prevent cross-contamination.

Precautionary efforts should also be considered when a DNAPL reservoir is encountered during drilling operations. The recommended approach is to cease drilling operations and install a well screen over the DNAPL zone and cease further drilling activities in the well. If it is necessary to drill deeper, construction of an adjacent well is recommended. Alternatively, if it is not necessary to screen off that interval, it is recommended to carefully seal off the DNAPL zone prior to drilling deeper.

Well construction material compatibility with DNAPL should be investigated to minimize downhole material failure. A construction material compatibility review and possible testing will prevent the costly failure of well construction material. The manufacturers of well construction material are likely to have the most extensive compatibility data and information available.

Remediation

Remediation of DNAPL mainly involves physical removal by either pumping or trench-drainline systems. Removal of DNAPL early in the remediation process will eliminate the main source of contaminants. This step will substantially improve the overall recovery efficiency of the various DNAPL phases including the long term pump and treat remediation efforts for soluble components. Remediation technologies such as vacuum extraction, biodegradation, ground water pumping, and soil flushing is mainly directed at the immobile DNAPL and the various phases in which its components occur. Physical barriers can be used in an effort to minimize further migration of the DNAPL.

Clean-up of DNAPL can involve sizable expenditures: they are difficult to extract and the technology for their removal is just evolving (43). Historically, field recovery efforts usually proceed with a poor understanding of the volume distribution of the DNAPL. This reflects the difficulties involved in adequate site characterization, poor documentation of the release, and the complexity associated with the DNAPL transport in the subsurface.

Pumping Systems

Pumping represents an important measure to stop the mobile DNAPL from migrating as a separate phase by creating a hydraulic containment and by removal of DNAPL (44). Very simply, DNAPL recovery is highly dependent on whether the DNAPL can be located in the subsurface. The best recovery scenario is one in which the DNAPL is continuous and has collected as a reservoir in a shallow, impermeable subsurface depression. Once the DNAPL has been located and recovery wells are properly installed, pumping of pure phase DNAPL is a possible option but depends largely on site specific conditions which include, but are not limited to: DNAPL thickness, viscosity, and permeability.

Many DNAPL reservoirs in the subsurface are of limited volume and areal extent. Therefore, it can be expected that both the level of DNAPL (saturated thickness) in the well will decline from the prepumping position and the percentage of DNAPL in the DNAPL:water mixture will decrease rather rapidly. Correspondingly, DNAPL recovery efficiency decreases. Field results indicate that recovery wells screened only in the DNAPL layer will maintain maximum DNAPL:water ratios (44). Well diameter was not found to influence long term DNAPL recovery; however, large diameter wells allow high volume pumping for short durations; and small diameter wells result in lower DNAPL:water mixtures and greater drawdown.

An enhanced DNAPL recovery scheme may be used to improve recovery efficiency. An additional well is constructed with a screen interval in the ground water zone located vertically upward from the DNAPL screen intake. Ground water is withdrawn from the upper screen which results in an upwelling of the DNAPL (70), refer to Figure 20. The upwelling of the DNAPL, coal tar in this case, improved the rate (twofold) at which the coal tar was recovered resulting in a more efficient operation. The ground water withdrawal rate must be carefully determined; too much will result in the coal tar from rising excessively and being either mixed (emulsions) with or suppressed by the higher water velocity above; too low will not

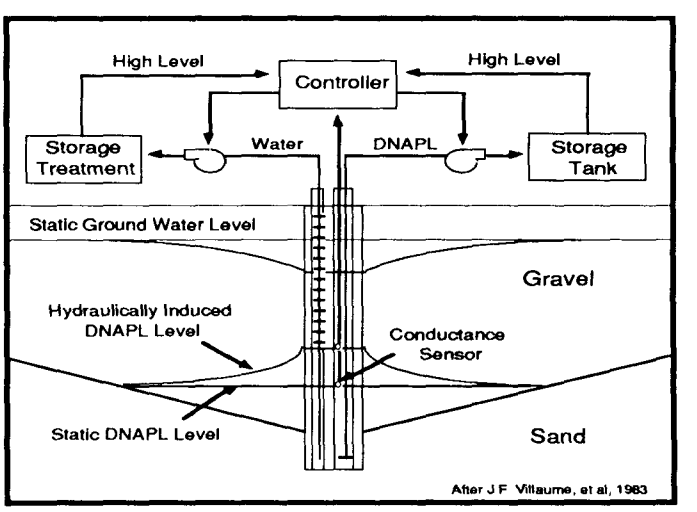

Figure 20. A DNAPL recovery system where deliberate upwelling of the static coal-tar surface is used to increase the flow of product into the recovery wells.

caused upwelling. An estimate of this upwelling can be calculated using the simplified Ghyben-Herzberg Principle under ideal conditions (4). Laboratory studies indicated that dimethyl phthalate (1.19 g/cc) recovery rate was doubled or tripled over the conventional, non-upconing, recovery scheme (75). A similar application of this technique was used to increase the level of DNAPL (solvents) in a sandstone bedrock formation (11). Other enhanced DNAPL recovery techniques were implemented utilizing both water flooding and wellbore vacuum. Essentially, this minimized drawdown, allowing a maximum pumping rate of the DNAPL:water mixture. Both techniques offered significant advantages in terms of the rate and potential degree of DNAPL removal (8).

The highly corrosive nature of some DNAPL's may increase maintenance problems associated with the recovery system. A design consideration during any DNAPL recovery program should include a material compatibility review to minimize downhole failures. This is applicable to the well construction material and the various appurtenances of the recovery system. Manufacturers of the construction material would most likely have the best compatibility information available.

While most scientists agree that the residual saturation of immiscible hydrocarbon droplets in porous media are immobile, researchers have investigated the mobility of residual saturation in porous media for enhanced oil recovery and for NAPL remediation at spill sites. Specifically, this includes a complex interplay between four forces (viscous, gravity, capillary, buoyancy). These forces are dependent on both the chemical and physical characteristics of the DNAPL and porous media. The mobilization of residual saturation mainly hinges on either increasing the ground water velocity which increases the viscous forces between the residual saturation and the ground water, or decreasing the interfacial tension between the residual saturation and the ground water which decreases the capillary forces.

The capillary number is an empirical relationship which measures the ratio between the controlling dynamic stresses (absolute viscosity and ground water velocity) and static stresses (interfacial tension) of the residual saturation (39). The former are the viscous stresses and the dynamic pressure in the water which tend to move the oil. The latter are the capillary stresses in the curved water/oil interfaces which tend to hold the oil in place. As the capillary number is increased, the mobility of the residual saturation increases. In a laboratory column study, the capillary number had to be increased two orders of magnitude from when motion was initiated to complete displacement of the hydrocarbon in a sandstone core (74). In a glass bead packed column, only one order of magnitude increase was required. However, a higher capillary number was required to initiate mobility. The difference in mobility between the two columns was attributed to the pore geometry, i.e. size, shape.

There are limitations to residual saturation mobilization. The ground water gradient (dh/dl) necessary to obtain the critical capillary number to initiate blob mobilization would be 0.24. To obtain complete NAPL removal would require a gradient of 18 (3). Ground water gradients of this magnitude are unrealistic. Another estimate of the gradient necessary to mobilize carbon tetrachloride in a fine gravel and medium sand was 0.09 and 9.0 respectively (74). The former gradient is steep but not unreasonable and the latter gradient is very steep and impractical to achieve in the field. The same researchers concluded from more recent, comprehensive studies, that the earlier predictions were optimistic, and that the gradient necessary to mobilize residual organic liquid is clearly impractical (66). Another limitation is that along with residual saturation mobilization, the NAPL blobs disperse into smaller blobs and that the blob distribution was dependent on the resulting capillary number (6). Recovery of the NAPL residual saturation by pumping ground water may be more feasible where the porous media is coarse and capillary forces are low, i.e. coarse sands and gravel. However, even in this scenario, it is expected that the radius of residual saturation mobilization would be narrow.

It is held in petroleum engineering theory that the only practical means of raising the capillary number dramatically is by lowering the interfacial tension (39) and that this can be achieved by using surfactants (66). Surfactants reduce the interfacial tension between two liquids, and therefore, are injected into the subsurface for enhanced recovery of immiscible hydrocarbons. In laboratory experiments, surfactant flushing solutions produced dramatic gains in flushing even after substantial water flushing had taken place (54). Unfortunately, surfactants can be quite expensive and cost prohibitive in NAPL recovery operations. Surfactants are usually polymeric in nature and a surfactant residue may be left behind in the porous media which may not be environmentally acceptable. Additionally, surfactants may be alkaline and thus affect the pH of the subsurface environment. It has been suggested that such a surfactant may inhibit bacterial metabolism and thus preclude subsequent use of biological technologies at the site. Significant research in this area is currently underway which may uncover information improving the economics and feasibility of this promising technology.

In summary, practical considerations and recommendations concerning the mobilization and recovery of residual saturation include the following: greater effectiveness in very coarse porous media i.e. coarse sands and gravel; recovery wells should be installed close to the source to minimize flow path distance; a large volume of water will require treatment/ disposal at the surface; compounds with high interfacial tension or viscosity will be difficult to mobilize; and implementation of linear one-dimensional sweeps through the zones of residual saturation (74) and surfactants will optimize recovery.

Pumping the soluble components (aqueous phase) of DNAPL from the immiscible (continuous and residual saturation), solid (sorbed), and gaseous phases has been perhaps one of the most effective means to date to both recover DNAPL from the subsurface and to prevent plume migration. Recovery of soluble components quite often has been the only remediation means available. This is largely attributed to the inability to locate DNAPL pools and due to low, DNAPL yielding formations. The basic principles and theory of pump and treat technology and the successes and failures have been summarized in other publications (64,67) and is beyond the scope of this publication.

Pumping solubilized DNAPL components from fractured rock aquifers historically has been plagued with a poor recovery efficiency. Although the rock matrix has a relatively small intergranular porosity, it is commonly large enough to allow dissolved contaminants from the fractures to enter the matrix

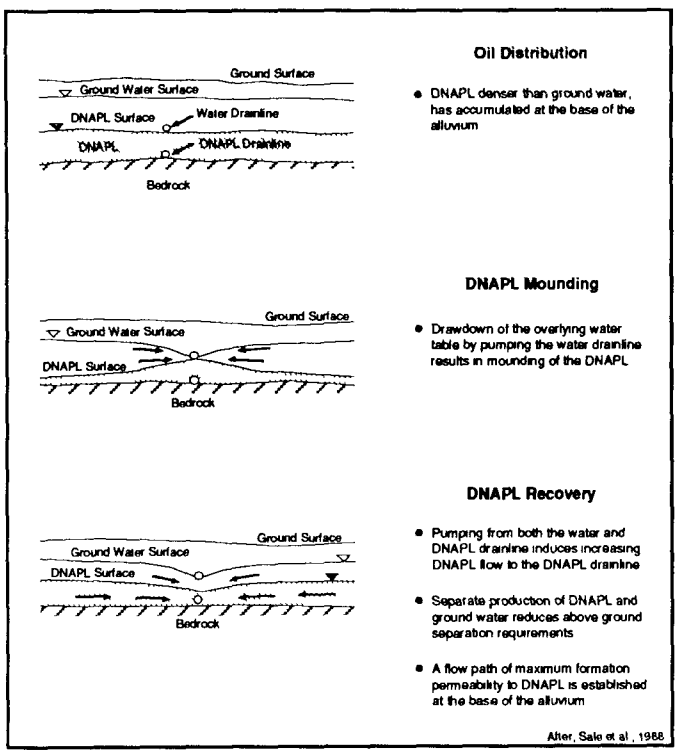

Figure 21. Trench recovery system of DNAPL utilizing the dual drainline concept.

by diffusion and be stored there by adsorption (32). The release of these components is expected to be a slow diffusion dominated process. This is because little or no water flushes through dead-end fracture segments or through the porous, impervious rock matrix. Therefore, clean-up potential is estimated to be less than that expected for sand and gravel aquifers.

Trench Systems

Trench systems have also been used successfully to recover DNAPL and are used when the reservoir is located near the ground surface. Trench systems are also effective when the DNAPL is of limited thickness. Recovery lines are placed horizontally on top of the impermeable stratigraphic unit. DNAPL flows into the collection trenches and seep into the recovery lines. The lines usually drain to a collection sump where the DNAPL is pumped to the surface. Similar to the pumping system, an enhanced DNAPL recovery scheme may be implemented using drain lines to improve recovery efficiency. This "dual drain line system" (41) utilizes a drain line located in the ground water vertically upward from the DNAPL line. Ground water is withdrawn from the upper screen which results in an upwelling of the DNAPL which is collected in the lower line, refer to Figure 21. This increases the hydrostatic head of the DNAPL. Excessive pumping of either single or dual drain line systems may result in the ground water "pinching off" the flow of DNAPL to the drain line. An advantage of the dual drain system is that the oil:water separation requirements at the surface are reduced.

Vacuum Extraction

Soil vacuum extraction (SVE) is a remediation technology which involves applying a vacuum to unsaturated subsurface strata to induce air flow. Figure 22 illustrates that the volatile contaminants present in the contaminated strata will evaporate and the vapors are recovered at the surface and treated. Common methods of treatment include granular activated carbon, catalytic oxidation, and direct combustion. SVE can effectively remove DNAPL present as residual saturation or its soluble phase components in the unsaturated zone. In general, vacuum extraction is expected to be more applicable for the chlorinated solvents (PCE, TCE, DCE) than the polycyclic aromatic compounds (wood preserving wastes, coal tars, etc.). When DNAPL is present in perched pools (Figure 12) it is more effective to remove the continuous phase DNAPL prior to the implementation of SVE. The same strategy is applicable in the saturated zone where DNAPL removal by SVE is attempted concomitantly with lowering the water table. Upon lowering the water table, SVE can be used to remove the remnant volatile wastes not previously recovered. Often, the precise location of the DNAPL is unknown; therefore, SVE can be used to remediate the general areas where the presence of DNAPL is suspected. Removal of DNAPL by SVE is not expected to be as rapid as direct removal of the pure phase compound. One advantage of SVE however, is that the precise location of the DNAPL need not be known.

Important parameters influencing the efficacy of SVE concern both the DNAPL and porous media. Porous media specific parameters include: soil permeability, porosity, organic carbon, moisture, structure, and particle size distribution. DNAPL specific parameters include: vapor pressure, Henry's constant, solubility, adsorption equilibrium, density, and viscosity (20). These parameters and their relationships must be evaluated on a site specific basis when considering the feasibility of vacuum extraction and a practical approach to the design, construction, and operation of venting systems (22). Additionally, soil gas surveys which delineate vapor concentration as a function of depth is critical in locating the contaminant source and designing an SVE system.

Historically, SVE has been used to remove volatile compounds from the soil. Recently it has been observed that SVE enhances the biodegradation of volatile and semivolatile organic compounds in the subsurface. While SVE removes volatile components from the subsurface, it also aids in supplying oxygen to biological degradation processes in the unsaturated zone. Prior to soil venting, it was believed that biodegradation in the unsaturated zone was limited due to inadequate concentrations of oxygen (17). In a field study where soil venting was used to recover jet fuel, it was observed that approximately 15% of the contaminant removal was from the result of microbial degradation. Enhanced aerobic biodegradation during SVE increases the cost effectiveness of the technology due to the reduction in the required above ground treatment.

Vacuum extraction is one form of pump and treat which occurs in the saturated zone where the fluid is a gas mixture. Therefore, many of the same limitations to ground water pump and treat are also applicable to vacuum extraction. While the application of vacuum extraction is conceptually simple, its success depends on understanding complex subsurface

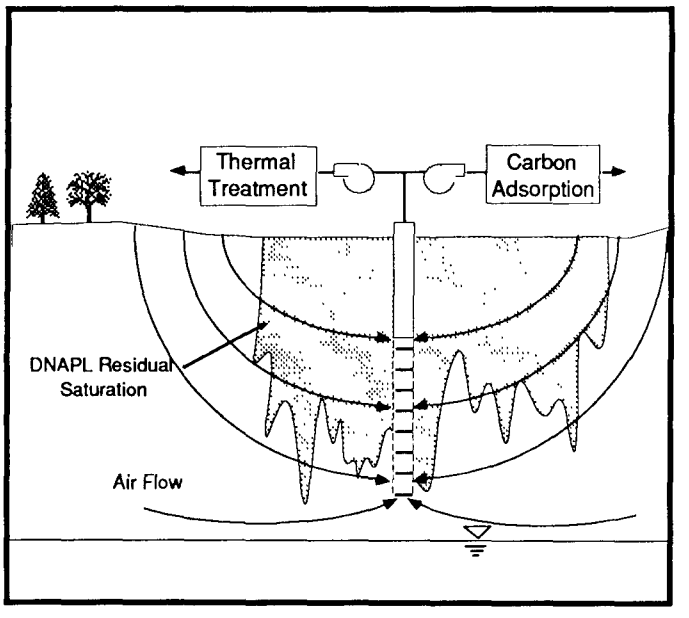

Figure 22. Vacuum extraction of DNAPL volatile components in the unsaturated zone. As shown here, vapors are treated by thermal combustion or carbon adsorption and the air is discharged to the atmosphere.

chemical, physical, and biological processes which provide insight into factors limiting its performance (9).

Biodegradation

The potential for biodegradation of immiscible hydrocarbon is highly limited for several reasons. First, pure phase hydrocarbon liquid is a highly hostile environment to the survival of most microorganisms. Secondly, the basic requirements for microbiological proliferation (nutrients, electron acceptor, pH, moisture, osmotic potential, etc.) is difficult if not impossible to deliver or maintain in the DNAPL. A major limitation to aerobic bioremediation of high concentrations of hydrocarbon is the inability to deliver sufficient oxygen. A feasible remediation approach at sites where immiscible hydrocarbon is present is a phased technology approach. Initial efforts should focus on pure phase hydrocarbon recovery to minimize further migration and to decrease the volume of NAPL requiring remediation. Following NAPL recovery, other technologies could be phased into the remediation effort. Bioremediation may be one such technology that could be utilized to further reduce the mass of contaminants at the site. NAPL recovery preceding bioremediation will improve bioremediation feasibility by reducing the toxicity, time, resources, and labor.

Similar to other remediation technologies, a comprehensive feasibility study evaluating the potential effectiveness of bioremediation is critical and must be evaluated on a site specific basis. A comprehensive review of biodegradation of surface soils, ground water, and subsoils of wood preserving wastes, i.e. PAH's (29,37,51,62,63) are available. A comprehensive review of microbial decomposition of chlorinated aromatic compounds is also available (58).

Soil Flushing

Soil flushing utilizing surfactants is a technology that was developed years ago as a method to enhance oil recovery in the petroleum industry. This technology is new to the hazardous waste arena and available information has mainly been generated from laboratory studies. Surfactant soil flushing can proceed on two distinctly different mechanistic levels: enhanced dissolution of adsorbed and dissolved phase contaminants, and displacement of free-phase nonaqueous contaminants. These two mechanisms may occur simultaneously during soil flushing (42).

Surfactants, alkalis, and polymers are chemicals used to modify the pore-level physical forces responsible for immobilizing DNAPL. In brief, surfactants and alkalis reduce the surface tension between the DNAPL and water which increases the mobility. Polymers are added to increase the viscosity of the flushing fluid to minimize the fingering effects and to maintain hydraulic control and improve flushing efficiency. Based on successful laboratory optimization studies where an alkali-polymer-surfactant mixture was used, field studies were conducted on DNAPL (creosote) which resulted in recovery of 94% of the original DNAPL (42). Laboratory research has also been conducted which indicated that aqueous surfactants resulted in orders of magnitude greater removal efficiency of adsorbed and dissolved phase contaminants than water flushing (55).

Depth to contamination, DNAPL distribution, permeability, heterogeneities, soil/water incompatibility, permeability reduction, and chemical retention are important factors when considering soil flushing (42). Prior to this technology being cost effective in the field, surfactant recycling will be necessary to optimize surfactant use (55). Soil flushing is complex from a physical and chemical point of view; is relatively untested in the field; and will likely be challenged regulatorily. Considerable research currently being conducted in this area may result in the increased use of this technology to improve DNAPL recovery in the future.

Thermal methods of soil flushing involve injecting hot water or steam in an effort to mobilize the NAPL. The elevated temperature increases volatilization and solubilization and decreases viscosity and density. A cold-water cap is used to prevent volatilization. The mobile phases of the DNAPL are then recovered using a secondary approach, i.e. pumping, vacuum extraction etc. This approach (Contained Recovery of Oily Wastes) to enhance recovery of DNAPL is currently under EPA's Superfund Innovative Technology Evaluation Program and a pilot-scale demonstration is forthcoming (21). A limitation in the use of thermal methods is that the DNAPL may be converted to LNAPL due to density changes (36). The adverse effects from this are that the DNAPL, existing as a thin layer, becomes buoyant and mobilizes vertically resulting in a wider dispersal of the contaminant. Other limitations involve the high energy costs associated with the elevated water temperature and the heat loss in the formation (36).

Physical Barriers

Physical barriers may be used to prevent the migration of DNAPL's in the subsurface and are typically used in conjunction with other recovery means. One feature of physical

barriers is the hydraulic control it offers providing the opportunity to focus remediation strategies in treatment cells. Unfortunately, physical barriers, while satisfactory in terms of ground water control and containment of dissolved-phase plumes, may contain small gaps or discontinuities which could permit escape of DNAPL (7). Chemical compatibility between physical barriers and construction material must agree to insure the physical integrity of the barrier. The history of the performance of these containment technologies is poorly documented and is mainly offered here for completeness of review. A more complete review of these physical barriers is available (5,56).

Sheet piling involves driving lengths of steel that connect together into the ground to form an impermeable barrier to lateral migration of DNAPL. Ideally, the bottom of the sheet pile should be partially driven into an impermeable layer to complete the seal. Slurry walls involve construction of a trench which is backfilled with an impermeable slurry (bentonite) mixture. Grouting is a process where an impermeable mixture is either injected into the ground or is pumped into a series of interconnected boreholes which together form an impermeable boundary. Again, the main feature of these techniques is to physically isolate the DNAPL.

In summary, site characterization and remediation options for sites containing DNAPL are limited. Field data from site characterization and remediation efforts are also limited. This is largely due to the complexity of DNAPL transport and fate in the subsurface, poorly developed techniques currently available to observe and predict DNAPL in the subsurface, and to the fact that this issue has not been widely recognized until recently. Clearly, there is a growing realization within the scientific and regulatory community that DNAPL is a significant factor in limiting site remediation. Correspondingly, current research efforts within the private, industrial, and public sectors are focusing on both the fundamentals and applications aspects of DNAPL behavior in subsurface systems. Additionally, the number of field investigations reflecting an increased awareness of DNAPLs, is growing.

DNAPL Modeling

A modeling overview report identified nineteen (numeric and analytic) multiphase flow models which are currently available (60). Most of these models were developed for salt water intrusion, LNAPL transport, and heat flow. Four models are qualitatively described as immiscible flow models but do not specifically indicate DNAPL. A more recent model has been developed which simulates density driven, three phase flow, that is capable of modeling DNAPL transport (23). Presently, very little information is available on DNAPL modeling in the scientific literature.

Multiphase flow modeling involves modeling systems where more than one continuous fluid phase (NAPL, water, gaseous) is present. Modeling any subsurface system requires a conceptual understanding of the chemical, physical, and biological processes occurring at the site. Modeling of simultaneous flow of more than one fluid phase requires a conceptual understanding of the fluids and the relationship between the fluid phases. The significance of multiphase flow over single phase flow is the increased complexity of fluid flow and the additional data requirements necessary for modeling.

As presented earlier, numerous variables strongly influence DNAPL transport and fate, and consequently, the mathematical relationship of these variables is complex. Therefore, it follows that DNAPL modeling presents paramount technical challenges.

Presently, it is exceedingly difficult to obtain accurate field data which quantitatively describes DNAPL transport and fate variables within reasonable economic constraints. DNAPL transport is highly sensitive to subsurface heterogeneities (8,27,28) which compounds the complexity of modeling. Heterogeneities are, by nature, difficult to identify and quantify and models are not well equipped to accommodate the influence of heterogeneities. Additionally, relative permeability and capillary pressure functions must be quantified to identify the relationship between fluids and between the fluids and the porous media. Unfortunately, these parameters are very difficult to measure, particularly in three phase systems. Prior to an investment of time and money to model a given site, a careful evaluation of the specific objectives and the confidence of the input and anticipated output data should be performed. This will help illuminate the costs, benefits, and therefore, the relative value of modeling in the Superfund decision making process.

In summary, DNAPL modeling at Superfund sites is presently of limited use. This is mainly due to: the fact that very little information is available in the scientific literature to evaluate previous work; accurate and quantitative input data is expected to be costly; the sensitivity of DNAPL transport to subsurface heterogeneities; and, the difficulty in defining the heterogeneities in the field and reflecting those in a model. However, multiphase flow models are valuable as learning tools.

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Appendix B

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Appendix C

DNAPL Workshop Agenda and Attendee Lists

DNAPL WORKSHOP
Dallas, Texas

April 16, 1991

INTRODUCTION

1:00 p.m.	Opening Remarks	Scalf
1:10 p.m.	OERR Perspective	Ankrum
1:30 p.m.	DNAPLs: Statement of the Problem with Emphasis on Low Viscosity DNAPLs	Cherry
2:10 p.m.	State of the Practice: High Viscosity DNAPLs	Villaume
2:40 p.m.	Current Regional Practices for Addressing DNAPLs	Willey
3:10 p.m.	A Perspective for DNAPL Assessment and Remediation	M. Mercer
3:40 p.m.	BREAK	

SITE CHARACTERIZATION: CURRENT STATE OF PRACTICE AND RESEARCH

4:00 p.m.	How to Determine Presence or Absence of DNAPLs in Groundwater	Feenstra
4:40 p.m.	Monitoring and Modeling DNAPLs	J. Mercer
5:10 p.m.	Geophysical Methods for DNAPL Detection	Olhoeft
5:40 p.m.	Delineation and Recovery of Mixed DNAPLs	Newell

April 17, 1991

REMEDIATION

8:00 a.m.	Current Options: An Overview	Cherry
8:30 a.m.	Pumping, Drains, Sumps	McWhorter
9:00 a.m.	Enhanced Recovery (High Viscosity)	Sale
9:30 a.m.	Enhanced Recovery (Low Viscosity)	Fountain
10:00 a.m.	BREAK	
10:30 a.m.	Vacuum Extraction for DNAPL Remediation	Johnson
11:00 a.m.	Heat/Steam (Above and Below Water Table)	L. Johnson
11:30 a.m.	In Situ Bioremediation	Sims
1:00 p.m.	Group Discussions--Site Characterization Options	Enfield
3:00 p.m.	BREAK	
3:30 p.m.	Group Discussions--Remediation Options	Cherry

April 18, 1991

8:30 a.m.	Continue Discussions Writing and Review Assignments
12:00 Noon	ADJOURN

DNAPL WORKSHOP ATTENDEE LIST

DALLAS, TEXAS
APRIL 16-18, 1991

Mr. Ted Ankrum	USEPA OSWER/OERR
Dr. John A. Cherry	University of Waterloo
Ms. Kathy Davies	USEPA, Region III
Ms. Lynn Deering	USEPA, OSWER/OERR
Dr. Ronald Drake	Dynamac Corporation
Mr. Neal Durant	USEPA, OSW/OSWER
Dr. Carl Enfield	USEPA, RSKERL
Mr. Stan Feenstra	Applied GW Research, Ltd.
Dr. John C. Fountain	University of Buffalo
Dr. Michael Henson	RMT, Inc.
Mr. Scott Huling	USEPA, RSKERL
Mr. Lyle Johnson	Western Research Institute
Dr. Rick Johnson	Oregon Graduate Institute
Dr. Dave McWhorter	Colorado State University
Dr. James W. Mercer	GeoTrans, Inc.
Mr. Mark Mercer	USEPA, Hazardous Site Control Div.
Mr. Paul Nadeau	USEPA, OSWER/OERR
Dr. Charles Newell	Groundwater Services, Inc.
Ms. Carolyn Offutt	USEPA, OSWER/OERR
Dr. Gary Olhoeft	USGS, Denver
Dr. Malcolm Pitts	Surtek
Dr. Paul Roberts	Stanford University
Mr. Randall Ross	USEPA, RSKERL
Mr. Tom Sale	CH_2M Hill, Inc.
Mr. Dick Scalf	USEPA, RSKERL
Dr. Steve Schmelling	USEPA, RSKERL
Dr. Ronald Sims	Utah State University
Dr. Nicholas Sitar	University of California, Berkeley
Ms. Jennifer Sutter	USEPA, OSWER/OERR
Dr. James Villaume	Pennsylvania Power & Light
Dr. James Weaver	USEPA, RSKERL
Mr. Dick Willey	USEPA, Region I
Dr. John L. Wilson	New Mexico Inst. of Mining & Tech.

Attendee List
DNAPL Workshop
Dallas, TX
September 5 & 6, 1991

University

Dr. John A. Cherry	University of Waterloo
Dr. Dave McWhorter	Colorado State University
Dr. John L. Wilson	New Mexico Tech.
Dr. Rick Johnson	Oregon Graduate Institute
Ms. Christina Hubbard	University of Waterloo
Ms. Sheryl Wilhelm	University of Waterloo

Consulting/Industry

Mr. Lyle Johnson	Western Research Inst.
Dr. James Mercer	Pres., GeoTrans, Inc.
Mr. Tom Sale	CH_2M-Hill, Inc.
Dr. Charles Newell	Groundwater Services, Inc.
Dr. Malcolm Pitts	Surtek
Dr. Michael Henson	RMT, Inc.
Dr. James Villaume	Pennsylvania Power & Light

U.S. EPA and USGS

Mr. Dick Willey	Region I
Ms. Kathy Davies	Region III
Ms. Lynn Deering	OSWER/OERR
Mr. Mark Mercer	OSWER/OERR
Ms. Jennifer Sutter	OSWER/OERR
Mr. Peter Feldman	OSW/OSWER
Ms. Penny Hansen	OSWER/OERR
Mr. Randall Breeden	OSWER/OERR
Ms. Carolyn Offutt	OSWER/OERR
Mr. John Smith	OSWER/OERR
Mr. Dick Scalf	RSKERL
Mr. Randall Ross	RSKERL
Dr. Carl Enfield	RSKERL
Dr. Steve Schmelling	RSKERL
Mr. Steve Acree	RSKERL
Dr. Dave Burden	RSKERL
Dr. Ellen Graber	Region VI
Dr. Gary Olhoeft	USGS

Dynamac/RSKERL

Dr. Ronald Drake	Dynamac

Appendix D

Glossary of Terms

The following terminology is intended to provide a consistent set of terms for use in discussions of investigations and remediation at DNAPL sites. The use of this terminology may avoid some of the confusion that commonly occurs when people from different backgrounds (hydrogeology, chemistry, reservoir engineering, regulatory, legal) attempt to discuss DNAPL issues or problems. This set of terms will probably warrant some revision after it is subjected to use in a multidisciplinary context.

Terminology for DNAPL Sites

CUTOFF WALL - A low-permeability vertical barrier placed around a zone of contamination. There are various types of walls, such as bentonite-soil slurry walls, concrete panel walls, plastic membrane walls, and sealable-joint steel sheet piling walls. The wall may be keyed into an aquitard (keyed wall) or not keyed (hanging wall).

DNAPL - An acronym for a dense nonaqueous phase liquid. It is synonymous with dense immiscible-phase liquid. The term has sometimes been used to refer to dissolved- or aqueous-phase contaminants, but to avoid confusion, the term DNAPL should be reserved exclusively for the nonaqueous phase liquid.

DNAPL ENTRY LOCATIONS - Locations where DNAPL has entered the subsurface by way of leaks, spills, discharges or any other escape.

DNAPL REMOVAL (or IMMISCIBLE-PHASE MASS REMOVAL) - Refers to removal of immiscible-phase residual, lens, or pools by technologies such as by free-phase pumping, water flooding, enhanced solubilization, vapor extraction or air sparging.

DNAPL SITE - A site where an immiscible liquid with a density greater than water has entered the subsurface and exists below the water table as a separate residual or immiscible phase.

DNAPL ZONE CONTAINMENT or IMMISCIBLE-PHASE ZONE CONTAINMENT - Refers to measures taken to control or prevent migration of dissolved-phase contaminants and immiscible-phase liquid (DNAPL). Plume control and DNAPL zone containment may involve some of the same remedial actions such as pumping well networks or drainage trenches, but the are generally applied in different areas.

FREE-PHASE LIQUID - Immiscible liquid existing in the subsurface under positive pressure. Free-phase liquid can flow into a well under the influence of gravity and can be mobilized by hydraulic forces.

GROUND-WATER REMEDIATION - A very general term referring to any or all activities taken to improve ground-water quality or control the spread of ground-water contamination, such as plume capture, or control, DNAPL removal or ground-water restoration.

GROUND-WATER RESTORATION - Refers to the removal of subsurface contamination to the degree necessary to achieve appropriate cleanup levels which protect public health and the environment.

GROUND-WATER ZONE - The zone below the water table or free water surface.

GROUND-WATER ZONE IMMISCIBLE PHASE - Immiscible phase in either the residual or free-phase state, present below the water table. Ground-water zone immiscible phase is particularly important at DNAPL sites because it is generally the primary cause of plumes of dissolved-phase chemicals. Permanent restoration of ground-water quality at DNAPL sites generally requires removal of essentially all the mass of ground-water zone immiscible phase.

IMMISCIBLE-PHASE ZONE or DNAPL ZONE - That portion of a site where immiscible-phase liquid exists as residual or free phase in the subsurface. This zone will also include chemical mass in the dissolved and sorbed phases. The immiscible-phase zone usually has immiscible-phase liquid both above and below the water table.

IN SITU IMMISCIBLE-PHASE DESTRUCTION - Refers to the destruction of DNAPL residuals, lens, or pools in situ by means of chemical or microbiological processes.

IN SITU IMMISCIBLE-PHASE SOLIDIFICATION - Refers to the immobilization of DNAPL residual, lens, or pools by physicochemical processes that solidify the DNAPL within the geologic medium, thereby preventing spread and/or dissolution of DNAPL in ground water.

LENS - A zone of free-phase liquid that rests on lower permeability strata of limited areal extent. A lens is a small perched pool. A "pool" and a "lens" are different only in scale.

PERMEABLE REACTION WALL - Is similar to a cutoff wall, but the wall is relatively permeable to allow unimpeded ground-water flow. The wall is partially constructed from reactive materials to destroy and/or sorb contaminants. A permeable reaction wall may be a passive alternative to pump-and-treat for plume control.

PLUME - The zone of ground-water contamination that exhibits dissolved-phase contaminants at concentrations above some specified concentration level, such as a drinking water limit, detection limit, or background. The volume of the subsurface that the plume encompasses includes the subsurface contaminant source (residual, lens, and pools of DNAPL). To avoid confusion, the term "plume" should not be used to refer to a pool of free-phase immiscible liquid. Plume removal refers to the removal of the dissolved-phase mass. DNAPL removal refers to removal of the immiscible-phase liquid.

PLUME CONTROL (or PLUME MIGRATION CONTROL) - Refers to measures taken to cutoff or control dissolved-phase contamination so that the advance of the plume is restricted, thereby reducing or eliminating the risk to receptors that would otherwise be impacted by dissolved-phase contaminants transported by ground water.

PLUME REMOVAL - Removal, generally, by pump and treat, of all or nearly all of a plume (except for dissolved-phase contamination in the immediate vicinity of DNAPL residuals, lens, or pools). Typically, at DNAPL sites, if the plume is removed and the pump-and-treat system is shut down, the plume will reestablish itself by dissolution of DNAPL located below the water table. Therefore, plume removal at DNAPL sites without containment (or removal) of the DNAPL zone will not achieve "ground-water restoration."

POLISHING - Polishing is a cleanup phase applied to remove or destroy dissolved, sorbed, or residual contaminants rather than immiscible-phase liquids in lens or pools. To achieve "ground-water restoration", an aquifer would generally need to be polished after other remedial measures have been taken to remove nearly all the mass of immiscible-phase (DNAPL) liquid.

POOL - A zone of free-phase immiscible liquid that resides at the bottom of an aquifer. A pool rests on top of an aquitard. A pool may be in an immobile state or it may be in a state of motion, depending on whether or not free-phase liquid is being added to the pool.

POOL or LENS REMOVAL -The removal of the free phase or otherwise movable immiscible liquid from a pool or lens by direct DNAPL pumping or enhanced mobilization. Such removal leaves a residual mass of immiscible-phase liquid under capillary tension.

PUMP-AND-TREAT - This term is reserved for the removal of water containing dissolved-phase contaminants by means of wells or trenches. The recovered water is treated at the surface.

RESIDUAL - Immiscible-phase liquid held in the pore spaces or fractures by capillary tension (negative immiscible-phase pressure). The immiscible-phase liquid in residual form cannot be mobilized by reasonable hydraulic forces.

SOURCE - This is a term meaning different things to different people. To some lawyers and administrators, source refers to surface or very near surface causes or potential causes of ground-water contamination, such as drums, sludge or contaminated surface soil. To scientists and engineers operating in the context of conceptual models of DNAPL in the subsurface, a source of most significance is generally a mass of immiscible-phase liquid (residual, lens, or pool) located below ground surface. To avoid confusion, the term "source" should be used with specific modifiers, such as below water table DNAPL source, surface source, etc.

VADOSE ZONE - The zone above the water table which may contain saturated or partially saturated sediments.

VADOSE ZONE IMMISCIBLE PHASE - Immiscible liquid present above the water table, generally as residual but occasionally as lenses of free-phase liquid perched on lower permeability strata.

VAPOR EXTRACTION - Refers to removal of DNAPL residuals, lenses, or pools by passage of air through vadose zone resulting in volatilization and gas transport.

VAPOR PLUME - Zone of vapor in the vadose zone.

*U.S. Government Printing Office: 1992 — 648-003/40719