



INTERSTATE TECHNOLOGY & REGULATORY COUNCIL

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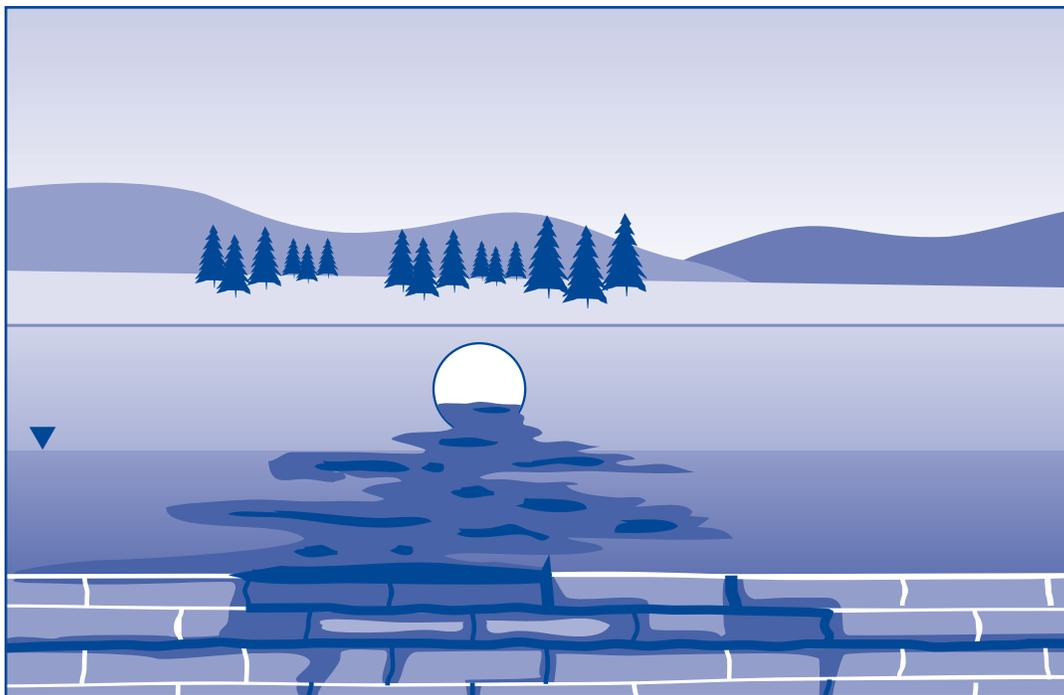


INTERSTATE TECHNOLOGY & REGULATORY COUNCIL



Regulatory Overview

DNAPL Source Reduction: Facing the Challenge



April 2002

Prepared by
Interstate Technology and Regulatory Council
Dense Nonaqueous Phase Liquids Team

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Established in 1995, the Interstate Technology & Regulatory Council (ITRC) is a state-led, national coalition of personnel from the environmental regulatory agencies of some 40 states and the District of Columbia; three federal agencies; tribes; and public and industry stakeholders. The organization is devoted to reducing barriers to, and speeding interstate deployment of, better, more cost-effective, innovative environmental techniques. ITRC operates as a committee of the Environmental Research Institute of the States (ERIS), a Section 501(c)(3) public charity that supports the Environmental Council of the States (ECOS) through its educational and research activities aimed at improving the environment in the United States and providing a forum for state environmental policy makers. More information about ITRC and its available products and services can be found on the Internet at www.itrcweb.org.

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Dense Nonaqueous Phase Liquids Team

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Dear Interested Party:

The ITRC DNAPL Team is pleased to issue our long-awaited regulatory overview document entitled *DNAPL Source Reduction: Facing the Challenge*. As acknowledged within, many people have contributed considerable time and effort to develop this document. The team developed this document as an overview of the complex technical and regulatory issues associated with DNAPL source reduction, and recognizes the controversy associated with the subject. While our goal is to see DNAPL sources cleaned up faster and more effectively, we acknowledge the technical difficulties and uncertainties surrounding the issue.

In recent months a number of scientific and policy panels have convened to discuss the pros and cons of DNAPL source zone treatment, including one at the ITRC Fall Conference held in Long Beach, California in November 2001. While these panels have illustrated the fractious nature and diversity of opinions on the topic, they have also shown that there are areas of agreement, particularly with regard to the need for additional, carefully developed cost and performance information.

Part of our future work will entail tracking over twenty demonstrations of innovative DNAPL treatment projects that are employing in situ thermal or chemical flushing. It is our hope that these demonstrations will begin to answer some of the technical questions regarding the value of such source reduction efforts. In addition, the team will be preparing three Technical/Regulatory Guidance Documents on DNAPLs, one on in situ flushing, one on DNAPL characterization strategies, and one on in situ thermal remediation.

The DNAPL Team invites you to periodically check the ITRC Web page at www.itrcweb.org to follow the progress of our future work.

Sincerely,

Eric Hausamann
ITRC DNAPL Team Leader

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DNAPL SOURCE REDUCTION: FACING THE CHALLENGE

1.0 INTRODUCTION

The ITRC DNAPLs (Dense Nonaqueous-Phase Liquids) Team was initially formed in 1999 to review several sampling and analysis plans commissioned by the Interagency DNAPL Consortium (IDC) and was later expanded to address emerging issues in DNAPL characterization and remediation. In 2000, the DNAPLs Team prepared a technology overview document summarizing recent developments in this field entitled *DNAPLs: Review of Emerging Characterization and Remediation Technologies* (ITRC, 2000).

The goal of the DNAPLs Team is to identify and reduce barriers to the deployment of technologies that efficiently treat DNAPL source zones. This document summarizes current regulatory attitudes toward DNAPL source zone remediation and outlines the pros and cons of partial source removal. Along the way, it challenges assumptions about the infeasibility of removing DNAPLs from certain geological settings where recent advances have made significant source reduction more feasible and cost-effective.

While our goal is to see DNAPL sources cleaned up faster and more effectively, we acknowledge the technical difficulties and uncertainties surrounding this issue. In recent months, a number of scientific and policy panels have convened for the purpose of discussing under what conditions DNAPL source zone treatment may be beneficial—and where it may have little or no impact. Although these panels have highlighted the fractious nature and diversity of opinions on this issue, areas of agreement have emerged, including the need to continue to develop the most promising technologies in the field so as to improve their predictability in terms of cost and performance. Also identified as an area for further research is the need to study the impacts of reduced source zone mass on groundwater quality and risk to human health and the environment. Providing answers to these questions should help reduce some of the uncertainty faced by decision makers at DNAPL sites. Therefore, we support the rigorous assessment of the performance of DNAPL source reduction technologies and encourage the collection and sharing of data from full-scale deployments of innovative DNAPL source zone treatment technologies.

Despite federal and state guidance citing the long-term benefits of source removal and recommending that DNAPL sources be remediated to the extent feasible (EPA, 1996), there is apprehension in the regulated community over the presumed high cost and uncertain benefit of aggressive source zone treatment. In certain situations, responsible parties can come away with a fear that, despite removing considerable DNAPL mass from the subsurface, little or no reduction in risk or regulatory relief will be realized. The result is that responsible parties and regulators alike can be “paralyzed into inaction” or retreat to the more conventional strategy of source zone containment as opposed to treatment. Partly for this reason, the remedial objective for the majority of sites with recalcitrant sources of DNAPL has been simply to contain the source material and prevent further contaminant migration.

Source containment systems have typically been based on groundwater extraction and treatment (pump and treat). While the up-front capital costs of installing an active hydraulic containment system may be more attractive from a net present value perspective as compared to the costs for source treatment, the estimated life-cycle costs of operating a typical pump-and-treat system for possibly 100 years or more are obviously considerable. In recent years, passive in situ source containment technologies, including permeable reactive barriers and enhanced biologically active zones, have been deployed that overcome some of the disadvantages of pump-and-treat systems. However, they still require long-term maintenance and don't hasten the reduction in DNAPL mass. Long-term costs associated with maintaining a permeable barrier may be lower.

This document describes some aggressive in situ technologies being deployed that target DNAPL source zones for elimination or substantial reduction in hopes of achieving more rapid remediation and speedier site closure. We recognize that many of these innovative technologies have not been sufficiently demonstrated (particularly in bedrock) to the point where they can be considered reliable or cost-competitive at this time. Therefore, we recommend that more studies be undertaken to evaluate their implementability and efficacy under a variety of geologic conditions and range of contaminants. Documenting these deployments through case studies to demonstrate the benefits and negatives of DNAPL source reduction is a short-term goal of the ITRC DNAPLs Team. These case studies will form the basis for technical/regulatory guidance documents and training modules to be produced in 2002 and 2003.

2.0 OVERVIEW OF THE DNAPL PROBLEM

It is generally agreed that cleaning up sites contaminated with DNAPLs presents one of the biggest challenges in the field of environmental remediation. This section presents an overview of the DNAPL problem and describes some of the technologies that have traditionally been employed to address these contaminated sites.

2.1 Behavior of DNAPLs in the Subsurface

DNAPLs are chemicals that exhibit a density greater than water and, therefore, tend to sink in the saturated subsurface environment. DNAPLs are also, by definition, hydrophobic (not very soluble in water), yet DNAPLs are soluble enough to present potential risks to human health or the environment. DNAPLs include the common industrial solvents tetrachloroethene (PCE) and trichloroethene (TCE), as well as other hazardous substances, like creosote and coal tar (Cohen and Mercer, 1993). Not ordinarily released into the environment as pure or neat chemicals, they are often discharged as spent solvents or wastes that contain appreciable fractions of other organic chemicals, such as other dense liquids or light mineral oils, or may be contaminants of light NAPLs. These other components can significantly influence the overall properties of the DNAPL and can both aid detection and complicate remediation.

When released in sufficient quantities in the unsaturated or saturated zone (either as a small, steady release or a large volume release), DNAPLs actively spread, primarily by gravity, until the free phase is distributed as a discontinuous mass of globules, or ganglia. This condition is commonly called *residual saturation*. The ultimate distribution of residual DNAPL is not uniform or predictable in the

subsurface due to minute variations in pore size distributions, soil texture, soil structure, and mineralogy. Although the residual DNAPL is immobile under normal subsurface conditions, it can act as a long-term source for continuing dissolution of contaminants into water or air in adjacent pores. If the downward movement of a DNAPL encounters low-permeability strata or large changes in permeability between layers in either the unsaturated or saturated zone, lateral spreading along the path of least resistance is promoted, in which case pools of free-phase DNAPL may accumulate along these boundaries. Except in large releases (such as may occur beneath petrochemical plants, pipelines, or tanks that produce, transport, or store industrial solvents), the formation of mobile, free-phase DNAPL pools is the exception rather than the rule (Cohen and Mercer, 1993).

Thus, investigators usually do not find free-phase DNAPL in soil cores or accumulating in monitoring wells using conventional characterization methods. Based on this lack of observable DNAPL, it is tempting to conclude that no DNAPL is present when in fact it may be present in substantial quantities at residual saturation. Reviewing the classic experiments of Schuille (1988) is valuable to gain an understanding of DNAPL behavior in the subsurface environment. Other helpful references are listed at the end of this document.

Another phenomenon, observed at some creosote sites, is that the specific gravity of the mixture can change over time. Some of the more soluble components can dissolve or are otherwise lost, and the NAPL mixture becomes less dense than water. Complex mixtures of NAPLs can also be found at former manufactured gas plant (MGP) sites in the form of plumes of semiviscous byproducts. These essentially neutrally buoyant components can readily migrate with groundwater as a separate phase fluid, further complicating the ability to map the subsurface contaminant distribution and predict its behavior.

2.2 Traditional Approaches to DNAPL Investigation and Remediation

What can be done to remediate a site suspected of having a DNAPL source? The most obvious answer, and one consistent with federal guidance on addressing sources of groundwater contamination, is to try to get it out of the ground. However, the mechanisms described above (active spreading, slow dissolution of the DNAPL components into groundwater, and potentially unpredictable migration) make DNAPLs extremely difficult to locate and quantify using conventional investigative techniques—and even more difficult to recover using “tried and true” technologies like groundwater pump and treat or soil vapor extraction. For instance, active pumping operations have been aborted at many DNAPL sites where groundwater concentrations have reached asymptotic levels, above health-based cleanup goals, due to the infeasibility of recovering more mass by continued pump and treat (National Research Council, 1994). Unable to restore groundwater to drinking water standards, the remedial objective prescribed for most DNAPL sites has been to prevent exposure to these materials by isolating the source and controlling further migration.

Locating DNAPL source areas. EPA defines sources as contaminated material acting as a reservoir for the continued migration of contamination to surrounding environmental media or as a source for direct exposure (EPA, 1991). With respect to DNAPLs, EPA defines the DNAPL zone as “that portion of the subsurface where immiscible liquids (free-phase or residual DNAPL) are present either above or below the water table” (EPA, 1996). Rarely are these liquids directly observed, yet evidence for DNAPLs exists at many sites. Generally, the presence of DNAPL has been inferred from

chemical data (e.g., the higher the aqueous or soil chemical concentration, the closer that point is to the source). The rule-of-thumb recommended by EPA is that DNAPL is likely present if the groundwater concentration of a particular contaminant exceeds one percent of its pure phase or effective solubility (EPA, 1992). The presence of DNAPLs has also been inferred from soil chemical data where the concentrations of DNAPL chemicals in soil are greater than one percent by mass or 10,000 ppm (EPA, 1994).

While data obtained from baseline soil and groundwater sampling may suggest the presence of DNAPL or the proximity to a source based on effective solubility or rules of equilibrium partitioning (Cohen and Mercer, 1993; Pankow and Cherry, 1996), these methods are location-specific and can fall short of enabling the investigator to locate and quantify the DNAPL source zone with a degree of understanding sufficient to design a remedial system. Although the investigator should collect samples of environmental media for laboratory analysis and visual inspection to evaluate the geosystem architecture within the source zone, more specialized and less-invasive techniques, many of which were described in the technology overview document (ITRC, 2000), should be considered earlier in the investigation to focus subsequent sample collection efforts.

Source treatment. Once a DNAPL source is identified or is suspected, a decision must be made regarding an appropriate remedial response. The National Oil and Hazardous Substances Pollution Contingency Plan (NCP), on which most federal and state cleanup programs are based, states that EPA expects to use “treatment to address the *principal threats* posed by a site, wherever practicable.” Principal-threat wastes, as defined by EPA, include “soils containing significant concentrations of highly toxic materials” (EPA, 1991) such as chlorinated solvents.

Treatment of DNAPL source zones implies removing DNAPL mass from the subsurface or destroying it in place; however, few technologies have demonstrated an ability to efficiently remove or destroy DNAPLs. Groundwater extraction, for instance, recovers only the dissolved fraction of the contaminant mass, which can be very small compared to the amount of residual or pooled DNAPL (Cohen and Mercer, 1993). Such an approach (groundwater extraction) is diffusion-limited and can take decades to recover the majority of the contamination. Source treatment technologies designed to extract and treat the dissolved phase (e.g., pump-and-treat systems), while effective at controlling contaminant migration, have been shown to be of limited effectiveness in reducing the mass of subsurface DNAPL (National Research Council, 1994). Unfortunately, alternatives to pump and treat for source treatment have historically been limited, which meant site managers were left with some form of containment remedy as the only feasible way of addressing DNAPL source areas.

Source containment. Partly due to the shortage of effective source treatment technologies, DNAPL sources have primarily been addressed by attempting to isolate the free phase and residual mass from the environment in order to minimize further contaminant flux to the groundwater. This isolation has been accomplished by constructing barriers of various types (e.g., slurry walls, sheet piling, or permeable reactive barriers) around the source zone but has more often been accomplished by establishing hydraulic control through extraction and treatment of groundwater from within the source area. Pump-and-treat systems can be very effective at containing dissolved-phase plumes emanating from source areas (EPA, 1999d). Their design and construction is relatively straightforward; and the resulting systems can be modified in the field to account for unforeseen or changing hydrogeologic conditions. The ability to incorporate such flexibility into the design of a

containment wall or other barrier is not as easy as with a pump-and-treat system—once a wall is emplaced, it is very difficult to modify, requiring a more thorough understanding of the geosystem prior to design in order to ensure that the source zone is encompassed as well as to avoid unwanted perturbation of the natural groundwater flow regime.

At some sites, these traditional approaches to controlling DNAPL sources through hydraulic containment or some form of physical barrier are being employed not as stand-alone remedies, but as important components of a robust DNAPL source removal and treatment train. For instance, a fail-safe groundwater extraction and treatment system can be critical as part of an aggressive source zone removal strategy (one involving enhanced mobilization) in order to prevent the spread of contamination beyond the treatment zone while the source is being treated.

3.0 DNAPL SOURCE REDUCTION: IS IT WORTH THE EFFORT?

This section revisits the issues of technical impracticability and the determination of what is feasible at DNAPL sites in light of recent successes of new, more aggressive in situ treatment technologies that have been demonstrated across the country. Arguments in support of deploying these technologies are presented and weighed against some of the technical, economic, and institutional barriers to their use, including the current lack of reliable cost and performance data.

3.1 Relevant EPA Policies

EPA has long recognized the complexity of remediating sites consisting of a nebulous DNAPL source and an associated groundwater plume (EPA, 1992). Restoring groundwater to health-based standards or to its beneficial use at sites with recalcitrant DNAPL sources can be very difficult and, using current technology, is often technically infeasible (EPA, 1993). In fact, there is a *presumption*, in some situations, that restoration is not feasible when DNAPLs are present (EPA, 1996). Of course, without adequate technologies or tools to feasibly remove DNAPLs from the subsurface and prevent further migration, containment is the only logical strategy to adopt. Associated with these technical challenges are institutional barriers, some of which are founded in dated policy that may be deterring attempts to remove more DNAPL source material.

Technical impracticability guidance. The Superfund Amendments and Reauthorization Act (SARA) of 1986 added Section 121(d) to CERCLA stipulating that the remedial standard or level of control for each hazardous substance, pollutant, or contaminant be at least that of any applicable or relevant and appropriate requirement (ARAR) under federal or state environmental law. In addition, an ARAR may be waived if it is technically impracticable from an engineering standpoint, based on the feasibility, reliability, and cost of the engineering methods required. For example, it may be technically impracticable to remove DNAPLs from a drinking water aquifer when it is trapped in deep bedrock fractures. The EPA or lead state agency may, in such cases, waive the requirement to meet ARARs yet still require that the source be contained. These are known as technical impracticability, or TI, waivers.

In 1993, EPA issued guidance that clarified how it determines whether groundwater restoration is technically impracticable (EPA, 1993). According to the TI guidance, DNAPL sites are the most likely types of sites to require TI waivers because of the limited number of DNAPL remedial technologies available (in 1993). EPA states that the long-term remediation objectives for a DNAPL zone should be to remove the free-phase, residual, and vapor-phase DNAPL to the extent practicable,” and that “removal of DNAPL mass should be pursued wherever practicable.” EPA also encourages the use of innovative technologies, where appropriate, to eliminate or isolate the DNAPL source zone, especially where the O&M costs associated with a conventional plume containment technology (like pump and treat) are prohibitive.

Some regulators believe that EPA’s TI guidance has discouraged more aggressive efforts by responsible parties to treat DNAPL source zones. For example, an OSWER Memorandum from 1995 (EPA, 1995) emphasizes that OSWER expects TI waivers will generally be appropriate for sites with contaminated groundwater where restoration to drinking water standards is technically impracticable, citing sites with DNAPLs as an example. The memo states, “Beginning immediately, RODs addressing DNAPL contamination that do not follow the policy in favor of TI waivers at such sites must include a written justification for that departure from this policy.” EPA also suggests in its presumptive response strategy for groundwater (EPA, 1996) that ARAR waivers due to technical impracticability will be appropriate for many DNAPL sites since “program experience has shown that removal of DNAPLs from the subsurface is often not practicable, and no treatment technologies are currently available that can attain ARAR or risk-based cleanup levels where subsurface DNAPLs are present.”

Things have changed in the past three to five years, and progress has been made in bringing innovative DNAPL extraction and treatment technologies to the hazardous waste market. As a result, what was infeasible a few years ago may be feasible today or in the near future. In short, our presumptions about DNAPL source zone remediation and decisions about feasibility must keep pace with emergent technology—ARARs should not be waived when accelerated groundwater restoration is a real possibility at a particular DNAPL site using these innovative technologies.

Monitored natural attenuation policy. Throughout the 1990s, natural attenuation received increasing attention as a cost-effective means of restoring contaminated groundwater where immediate threats to public health from drinking contaminated groundwater did not exist. Inevitably, natural attenuation began to be perceived by many as a “walk-away” approach to achieving remedial objectives at a site. EPA published its monitored natural attenuation (MNA) policy directive (EPA, 1999a) in part to assure skeptics and critics of MNA that EPA does not consider MNA, when applied appropriately, as a “no action” approach. MNA can be protective when it can attain remedial objectives in a *reasonable time frame* and the prescribed data collection protocols are followed. The remedial time frame is dependent on site-specific conditions, including the nature and extent of groundwater contamination, usability of the aquifer, existing and potential future impact on human and environmental receptors, existing and potential development of the area, and the availability of a public water supply. EPA acknowledges the potentially adverse effect of residual NAPL and other contaminant sources on remedial time frames and, therefore, recommends that, particularly at sites where MNA is under consideration, remedial actions include the removal and treatment of source materials. Preference is given to removal or treatment of “principal-threat wastes,” including NAPL solvents (EPA, 1999a).

EPA's technical protocol for evaluating natural attenuation of chlorinated solvents also advocates NAPL source removal, treatment, or containment to shorten the time frame needed for natural processes to attain remedial objectives (EPA, 1998). The document recommends that "where removal of mobile NAPL is feasible, it is desirable to remove this source material and decrease the time required to reach cleanup objectives. Where removal or treatment of NAPL is not practicable, source containment may be practicable and necessary for MNA to be a viable option" (EPA, 1998).

3.2 Pros and Cons of Source Reduction

Currently, there is a scientific debate raging over whether removal of DNAPL mass from the subsurface is warranted. Eminent practitioners and scientists on both sides of the "utility vs. futility" issue can point to select studies that find that removal of DNAPL mass has either a significant impact on groundwater quality or a negligible impact. In most cases, the findings are site-specific and narrow in their applicability. Thus, the conclusions are difficult to apply to other sites and geologic conditions. In this section, we attempt to contrast the arguments supporting aggressive DNAPL source reduction with those favoring the more conventional approach that relies on containing the source.

3.2.1 Benefits of Source Reduction

Shorter remedial time frames. By aggressively attacking the heart of the DNAPL mass, while managing the dissolved-phase groundwater plume down gradient of the source, contractors can, it is argued, shorten the time frame for the ultimate cleanup of the site (not just the conditional attainment of MCLs down gradient of some hydraulically isolated source area) and reduce long-term operation and maintenance costs. Estimates of the time it would take to achieve health-based groundwater standards, for instance, under a pump-and-treat scenario can be upwards of 500 years for some recalcitrant sources, due to the fact that the recovery of residual DNAPL mass through pumping is limited by the slow rates of dissolution of partially soluble compounds into the dissolved phase and by diffusion out of low-permeability beds. By comparison, the application of robust chemical, thermal, and even biological treatment technologies aimed directly at the source of contamination may dramatically enhance the recovery rate of DNAPL mass (through traditional groundwater or vapor extraction methods) by enhancing the DNAPL's solubility and/or its rate of diffusion. As source material is removed, the argument goes, attenuation of the residual groundwater plume is hastened and the path to site closeout is shortened (EPA, 1998).

Elimination of long-term operation and maintenance. In the absence of technologies capable of effectively treating DNAPL sources, cleanup efforts have focused on eliminating down-gradient exposures to contaminated groundwater by remediating the dissolved plume and containing the source. Containment of the DNAPL source typically involves employing hydraulic control or some form of physical barrier that requires long-term operation and maintenance. Extensive monitoring of groundwater quality outside the source containment system is also required to assess the performance of these engineered systems and prevent leakage. Without effective removal or treatment of the source, the need for such long-term operation, maintenance, and monitoring could extend into perpetuity.

Less restrictions on future use. During the time that pump and treat or other containment-oriented remedies are operating at a site, the use of groundwater or other human activities is often restricted through institutional controls or other restrictions. If source removal results in achievement of remedial objectives sooner, then the institutional controls needed to prevent exposure can be removed earlier. Further, since ongoing remediation is not required (or can be shut down sooner), the space that the system would have occupied is available for use. Elimination of “principal-threat wastes,” including DNAPLs or other potential sources of groundwater contamination, can also serve to reduce the long-term liability associated with a property. These factors may result in a quicker return of the site to productive use with fewer restrictions.

Consistent with regulatory goals. Many states acknowledge the benefits of source removal as a prerequisite to implementing MNA. South Carolina, for instance, requires that the source of the groundwater contamination must be removed, remediated, and/or contained with respect to sites proposing MNA. A basic tenet of New York’s groundwater remediation strategy is source removal—where an identifiable source of groundwater contamination exists, one of the primary remedial objectives is to remove or eliminate the source to the extent feasible. Florida regulations governing the state’s dry cleaner and brownfield programs provide regulatory flexibility by supporting less aggressive dissolved-plume remedial approaches, such as MNA or permeable reactive barriers, in conjunction with aggressive DNAPL source removal. The goal of reducing DNAPL source mass is also consistent with EPA’s MNA policy, which advocates source removal, containment of the residual source, modeling to show that additional active remediation is not required, and monitoring to track improvements (EPA, 1999a). In addition, source removal and/or treatment of DNAPLs is one of the Early Actions recommended by EPA as a presumptive response for contaminated groundwater at sites with suspected DNAPL (EPA, 1996).

3.2.2 Barriers to DNAPL Source Reduction

Although new technologies are emerging for cleaning up DNAPL sources (especially in porous media), a significant amount of resistance to their use exists within the remedial community, representing barriers to their implementation. Much of this resistance stems from the view that these new technologies are very expensive and unpredictable in their performance.

Lack of reliable cost and performance data. Like most developing technologies, cost and performance data from full-scale applications of these aggressive DNAPL cleanup technologies are scarce. According to those subscribing to this argument, it is unlikely that responsible parties will elect to aggressively remove DNAPL mass until these technologies are fully proven and predictions of their cost and performance can be made with greater certainty under specific geologic conditions.

Potential for uncontrolled migration. Because many of the aggressive treatment technologies rely on increasing the mobility of the DNAPL—either by a phase change from liquid to vapor, a reduction in viscosity, or by an increase in solubility—there is the potential for uncontrolled mobilization and spreading of contamination, a factor that must be accounted for in the design.

Uncertain impact on groundwater. There is very little data from the field about the impact source mass reduction has on long-term groundwater quality. For example, evidence is scanty that eliminating most but not all the DNAPL mass from a source zone results in a shorter remedial time

frame (as is evidence for the counterargument, that DNAPL source mass removal has no effect). As we have learned, DNAPLs comprise a class of essentially recalcitrant, hydrophobic contaminants. Even small amounts of residual DNAPL can contaminate very large volumes of water for long periods. The prospect of incomplete removal of the source while leaving residual DNAPL behind is, therefore, a real possibility. For instance, what would happen if 70% or 80% of the DNAPL mass was removed by an aggressive method, but no noticeable improvement in groundwater quality resulted after a year of monitoring? More than likely, a containment remedy would need to be implemented until the remaining source material was degraded sufficiently. One could argue that the significant investment of energy and capital to remove only a portion of the DNAPL source mass would have been wasted since a pump-and-treat system (or other containment remedy) was required anyway.

Regulatory and institutional resistance. Although there are certainly real technical and economic impediments standing in the way, a fair amount of apprehension concerning whether or not to go down the DNAPL source reduction path must also be attributed to the failure to let go of dated assumptions and policies concerning what is feasible. There is also the fear of making things worse by spreading DNAPLs around and perhaps turning regulators into problem holders.

4.0 NEW APPROACHES TO DNAPL SOURCE ZONE REMEDIATION

This section discusses some of the more promising in situ technologies for characterizing and remediating DNAPL source zones. It is important to note that the applicability of these technologies to specific situations depends on the type of DNAPL present, the site geology, and the remedial objective established for the project. Each technology will have its own niche, and ITRC is not suggesting that these technologies can be applied universally to all DNAPL sites.

4.1 New Tools for Characterizing DNAPL Source Areas

One of the most challenging and important tasks in the design of a DNAPL remedy is to sufficiently characterize the subsurface DNAPL distribution at the site to allow the selected remedial technology to be successful. DNAPL distribution is difficult to delineate accurately at many sites because DNAPLs migrate preferentially through selected pathways (e.g., fractures and coarse sand layers) and are affected by small-scale changes in the stratigraphy of an aquifer (EPA, 1992; Pankow and Cherry, 1996). Being able to predict the fate and transport of DNAPLs under natural conditions is desirable since these same migration pathways are often put to use as pathways for enhanced DNAPL extraction during the remedial phase. However, the investigator should be careful not to “over-characterize” a site. In other words, the scope of the source area investigation should be appropriately sized based upon the particular needs of the remedial technology to be employed. As such, the investigation of DNAPL sites may require a site-specific approach or conceptual basis to successfully characterize the site and implement an effective remedial action.

4.1.1 The Toolbox Approach

The overall understanding of DNAPL sites can be made more precise and efficient by using an appropriate combination of innovative characterization tools and conventional methods of sample

collection and analysis. Such a *toolbox approach* to DNAPL characterization can add flexibility and help to offset some of the limitations to using traditional methods alone (Rossabi et al., 2000). Conventional methods of locating DNAPL in the subsurface have included groundwater monitoring wells, multilevel samplers, soil gas measurements, chemical analysis of soil samples, and soil borehole logging to determine site stratigraphy. Although these methods can be reliable for quantifying DNAPL concentrations and mass in a previously identified source zone, there is the potential to miss discrete pockets of DNAPL contamination in the subsurface, which can lead to incomplete characterization and, depending upon the robustness of the remedy, inadequate remedial designs. For example, at Hill Air Force Base, a containment wall was constructed around a DNAPL source area that had not been adequately characterized. Subsequent monitoring showed that most of the DNAPL mass was outside the perimeter of the wall (USAF, 1999; Brown et al., 1998). In addition, extreme care must be exercised when using techniques that require drilling into the subsurface since the practice can result in the creation of new pathways for downward migration of free-phase DNAPLs (EPA, 1994).

A toolbox approach to DNAPL characterization was used by investigators at the Savannah River Site, where an integrated suite of traditional and innovative characterization technologies was put to use, providing valuable information on the site geology and distribution of DNAPL (Rossabi et al., 2000). The acceptance of DNAPL investigations that incorporate innovative characterization approaches is vital to successfully deal with the unique nature and challenges of DNAPL.

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

4.1.2 Innovative Characterization Tools

Several innovative techniques for characterizing the subsurface distribution of DNAPLs were presented in the technology overview document (ITRC, 2000) and are briefly reiterated below. These characterization technologies may provide alternatives for overcoming the limitations and expense of traditional drilling programs. Kram *et al.* recently compared the performance of various DNAPL characterization methods and approaches, including the innovative tools discussed in this section (Kram *et al.*, 2001). Appendix A summarizes, in matrix form, some of the innovative tools that can be incorporated into various stages of DNAPL site investigations.

Direct Push Technologies. Recent advances in cone penetrometer and sensor technology have enabled DNAPL sites to be rapidly characterized using vehicle-mounted direct push probes. Probes are available for directly measuring contaminant concentrations in situ, in addition to measuring standard stratigraphic data, to provide flexible, real-time analysis. The probes can also be reconfigured to expedite the collection of soil, groundwater, and soil gas samples for subsequent laboratory analysis.

Geophysical Technologies. Noninvasive, geophysical technologies addressed in the earlier document include ground-penetrating radar (GPR), cross-well radar, electrical resistance tomography (ERT), vertical induction profiling, and high-resolution seismic reflection. They typically produce computer-generated images of subsurface geological conditions and are qualitative at best. These techniques do not directly detect or map DNAPL, but they can be useful in characterizing and differentiating the various geologic units to estimate the likely distribution of DNAPLs and guide subsequent sampling by more invasive methods.

Other Approaches. Chemical tracers are being used to identify and quantify residual DNAPL zones, based on their affinity for a particular contaminant and the measured change in tracer concentration between wells employing a combination of conservative and partitioning tracers. The Ribbon NAPL Sampler is a qualitative tool for detecting DNAPLs, which consists of a dye-impregnated flexible liner that reacts to the presence of DNAPLs in an open borehole.

4.2 Innovative Approaches to Source Zone Reduction

This section provides an overview of some potentially viable technologies to eliminate or greatly reduce DNAPL mass at the source. Given that these emerging technologies are becoming more commercially available and have proven successful to some degree (although primarily in porous media), source containment may no longer be the preferred way to mitigate DNAPL at some sites. It is important to note, however, that in some cases, a containment strategy alone may best serve the needs of the project, depending on the hydrogeologic setting and other factors that might weigh against DNAPL zone treatment.

4.2.1 Integrated Remedial Strategy

Recently, some researchers have begun advocating an integrated or phased strategy to remediating sites with DNAPLs that is based on aggressive source removal combined with less aggressive alternatives for managing the dissolved plume (Rao, *et al*, 2001). At many sites with DNAPL source zones and associated groundwater plumes, natural attenuation is currently acting to reduce contaminant concentrations in groundwater down gradient of the source. Under certain conditions (even with DNAPLs present), MNA can be a viable alternative to active remediation (such as pump and treat) for aquifer restoration or to prevent unacceptable exposures. However, a monitored, naturally attenuating plume alone does not warrant selection of an MNA remedy if the length of time required to reach cleanup objectives is not reasonable due to an active DNAPL source zone. In such cases, MNA probably will not be an effective component of the remedy until the DNAPL source is isolated or removed (EPA, 1998).

Many practitioners believe that aggressive treatment of the DNAPL source zone to the point where natural attenuation processes, or other passive technologies, are able to efficiently treat the residual concentrations should accelerate site closeout and reduce life-cycle costs. Through fate and transport modeling, the benefit of isolating the source from the environment (via treatment or containment) can be shown theoretically by decreasing the source term and modeling the effects on the remedial time frame for the residual plume (EPA, 1998). Source control or containment may be necessary in the interim to minimize contaminant flux to the groundwater and recover mobilized DNAPLs while aggressive source treatment is occurring. However, it is anticipated that such a requirement would be temporary. Further research and field data testing of this hypothesis need to be completed, however.

4.2.2 DNAPL Source Reduction Technologies

This section describes some innovative DNAPL remediation technologies, including a few technologies designed to enhance contaminant extraction and some that enhance contaminant destruction. Appendix B is a matrix containing further information on these technologies.

Steam Enhanced Extraction. Steam Enhanced Extraction (SEE) uses an alternating steam injection and vacuum extraction approach to remove volatile components from the soils in the vadose zone. The process of heating the subsurface, using either steam or electrical energy, enhances the vapor extraction process by increasing vapor pressure and volatilization rates of organic compounds in the soil. It also results in reductions of viscosity and residual saturation of semivolatile and nonvolatile compounds, which causes greater mobility and, consequentially, greater removal efficiency of separate-phase hydrocarbon. These two mechanisms also apply to the major DNAPL groups—chlorinated solvents (enhanced volatility) and creosote (viscosity reduction and enhanced mobility).

Dynamic Underground Stripping. Dynamic Underground Stripping (DUS) is an in situ thermal technology, developed by researchers at the University of California, Berkeley and LLNL, that combines steam injection and electrical resistance heating for aggressive DNAPL source reduction. DUS is applicable for two groups of contaminants: volatile and semivolatile/nonvolatile organic compounds.

Electrical Resistance Heating. Electrical resistance heating (ERH) is a poly-phase, electrical technology that uses electrical resistive heating and in situ steam production to accomplish subsurface remediation. Electrical energy is delivered to the subsurface by vertical, angled, or horizontal electrodes installed using standard drilling techniques. Because the ERH electrodes are electrically out of phase with each other, electrical current flows from each electrode to all the other adjacent out-of-phase electrodes. It is the resistance of the subsurface to this current movement that causes heating. The result is a uniform subsurface heating pattern that can be generated in both the saturated or vadose zones. Electricity takes the pathways of least electrical resistance when moving between electrodes, and these pathways are heated preferentially. Through preferential heating, ERH creates steam from within saturated silt and clay stringers and lenses as well as cracks in the bedrock. The physical action of the steam escaping these fracture flow pathways and tight soil lenses drives contaminants out of what is otherwise diffusion-limited portions of the soil matrix.

Thermal Conduction. The aforementioned in situ thermal technologies are designed primarily to enhance the extraction of contaminants, either through volatilization or removal as separate-phase hydrocarbons. By contrast, heating the subsurface via in situ thermal conduction, which simultaneously applies heat to the soil by a combination of thermal conduction and vacuum, heats the soil to temperatures *above* the boiling point of water to destroy most (95%–99% or more) of the contaminant mass while still in the ground. The remaining vapors are collected and treated above ground. This patented thermal conduction technology is applicable to all organic contaminants (volatile, semivolatile, and nonvolatile) and has been demonstrated to achieve stringent cleanup goals, even for high boiling point contaminants such as PCBs, PAHs, pesticides, dioxins, nitroaromatics, and heavy hydrocarbons, as well as for lower boiling point contaminants such as TCE, PCE, and gasoline and diesel fuel (Stegemeier and Vinegar, 2000).

In Situ Chemical Flushing. In situ chemical flushing describes an approach to enhanced DNAPL removal involving the injection and subsequent extraction of chemicals to solubilize and/or mobilize DNAPLs. The chemicals are injected into a system of wells designed to “sweep” the DNAPL zone within the aquifer. The chemical “flood” and the solubilized or mobilized DNAPL is removed through strategically placed extraction wells, and the produced liquids are then treated and either disposed or returned to the subsurface. The chemicals used are typically aqueous surfactant solutions or cosolvents (e.g., alcohols). In the former case, the process is referred to as Surfactant-Enhanced Aquifer Remediation, or SEAR; in the latter case, it is referred to as cosolvent flooding. Both chemicals lower the interfacial tension between DNAPL and the chemical flood. Both surfactant and cosolvent flooding have been applied at full scale in the field.

In Situ Enhanced Desorption and Bioremediation. Biological desorption and degradation refers to the use of in situ biological activity to treat contaminants, including chlorinated contaminants present as residual DNAPLs. In this process, electron donor substrates are introduced into the subsurface, stimulating native microbes to degrade dissolved contaminants through the process of reductive dechlorination. Nonindigenous microbes may also be introduced into the subsurface. This, in turn, induces a steep dissolution gradient, forcing residual DNAPL to desorb from the aquifer matrix into the dissolved phase and subsequently degrade through reductive dechlorination. Direct evidence of rapid biological desorption and degradation of DNAPL has been presented recently (Carr, et al, 2000; Koenigsberg et al, 2001). Field application of biological desorption and degradation technology for chlorinated residual DNAPL has been demonstrated at several sites employing a slow-release electron donor.

In Situ Chemical Oxidation. Remediation of contaminant source areas using in situ chemical oxidation (ISCO) involves injecting oxidants and other amendments as required directly into the source zone. The first documented evaluation of in situ chemical oxidation using potassium permanganate to treat DNAPLs was in 1994 (Schnarr et al, 1998). Three of the most common chemical oxidants used for ISCO are permanganate (either sodium or potassium permanganate), hydrogen peroxide, and ozone. The injected oxidants react with the contaminant, breaking chemical bonds and producing innocuous substances such as carbon dioxide, water, and chloride (ITRC, 2000). ISCO technology is described in greater detail in a technical and regulatory guidance document developed by ITRC’s In Situ Chemical Oxidation Team (ITRC, 2001).

5.0 PATH FORWARD

This document is part of an ongoing process to reduce barriers to the deployment of DNAPL treatment technologies through technical and regulatory innovation. We have discussed potential benefits of removing or significantly reducing DNAPL source mass but recognize that most of the innovative technologies available for aggressively attacking these source zones, particularly in bedrock, have not been adequately demonstrated to the point where implementation is routine. More studies need to be completed to evaluate their implementability and efficacy under a variety of geologic conditions.

5.1 Economics of Source Mass Reduction

Many states, including those represented on the DNAPLs Team, believe that DNAPL source mass reduction, where feasible and appropriate, should be an integral part of a site's comprehensive groundwater remediation strategy, particularly where it can be demonstrated that the source reduction effort will have a positive affect on the remedial time scale and accelerate site closeout.

From an economic standpoint, the question is whether a shorter remedial time frame translates to lower life-cycle costs when compared to the cost of long-term containment. Deploying any of the aggressive source reduction technologies described in this document is relatively expensive, *in the short-term*. And while it may be feasible to remove or destroy a significant mass of DNAPL, contaminants in groundwater near the source will likely remain for some period and may still require active remediation or containment to protect public health and the environment. As we have suggested, the best use of these technologies may be as part of a treatment train, combining aggressive source reduction, plume control, and passive restoration, which will hopefully place the project on a faster track to site closeout.

When evaluating the cost of groundwater remedies at sites with known or suspected sources of DNAPL, emphasis should be placed on determining how much source material can be removed or destroyed before reaching a point of diminishing returns. In other words, what is the most cost-effective combination of aggressive source reduction and dissolved plume management? If complete removal of the DNAPL source results in restoration of an aquifer to beneficial use, for example, then that greater benefit and its associated costs should be included in the cost-benefit analysis. Such an analysis must also consider the real, long-term cost of *not* aggressively attacking the DNAPL source by addressing only the dissolved-phase plume. Perhaps the most compelling reason for attempting source reduction is the prospect of avoiding the cost of long-term operation and maintenance (O&M) and the liabilities associated with traditional source containment remedies.

The current data indicate that, in general, pump-and-treat systems when applied to sites with recalcitrant DNAPLs are not very effective at mass removal (National Research Council, 1994) but are effective at containing a plume. Compared to the total costs of operating these systems as long-term groundwater remedies (in some cases for decades or even centuries), the aggressive DNAPL source reduction approaches discussed in this document may become even more economically attractive. The bottom line is that there are certain situations where the higher initial expenditures of deploying aggressive source reduction technologies are justified and offset by the elimination or minimization of long-term O&M costs. However, the jury is still out as to what those situations are. More data from field deployments need to be collected to determine the economics of source zone remediation and to minimize this uncertainty.

5.2 State Regulatory and Policy Perspective

Many states encourage the aggressive cleanup of DNAPL source areas to the extent feasible. This policy is consistent with federal EPA guidance, which advocates source treatment where practicable. This section outlines the regulatory and policy positions of several states regarding DNAPL source areas and offers some ways in which the “sticker shock” often associated with aggressive source reduction proposals might be eased.

Guiding Principles. The following statements summarize the regulatory positions of many states, including those on the DNAPLs Team:

- C Investigators should make use of innovative DNAPL characterization tools and approaches, when appropriate and cost-effective. Due to the unique nature and challenges of locating DNAPLs, traditional investigative methods have not provided adequate understanding of DNAPL source zones and should be supplemented with more effective methods.
- C DNAPL source mass reduction should be encouraged in an effort to accelerate restoration and reduce life-cycle costs, through greater flexibility in enforcing technical and regulatory requirements for down-gradient plume restoration, as long as human health and the environment are not impacted.
- C Free-phase DNAPL that can be readily pumped or bailed from the subsurface within a reasonable time frame should be removed to the extent feasible.
- C To the extent feasible, residual DNAPL should be removed or treated in situ to the point where it no longer constitutes a continuing source of groundwater contamination or the rate of natural attenuation exceeds the rate at which contaminants are entering the dissolved phase.
- C ARAR waivers due to technical impracticability should not be granted for DNAPL sites without serious consideration of innovative and emerging source reduction technologies.
- C Reduction of the DNAPL source, including removal or treatment of free-phase and residual DNAPL, should be considered an integral part of a presumptive response strategy for contaminated groundwater.

Regulatory Flexibility. While states generally advocate removal or treatment of DNAPL sources, we recognize that it can represent a huge shock to a company's short-term financial outlook compared to the costs of a long-term source containment approach. As an incentive for the aggressive removal of DNAPL source mass, regulators could reward such efforts, where feasible, by accepting less aggressive strategies for the down-gradient plume, such as MNA. Regulatory agencies can provide flexibility by supporting less aggressive dissolved-plume remedial approaches in conjunction with aggressive DNAPL source removal, as long as the overall remedy remains protective of human health and the environment. For example, Florida has developed a table of default groundwater cleanup criteria, or Natural Attenuation Default Concentrations (NADCs), applicable to source zone remediation, which are 10 to 100 times the state's groundwater criteria in order to encourage source reduction. These NADCs serve as *de facto* remedial action objectives for groundwater source areas below which it is assumed that groundwater will attenuate naturally to meet standards.

To promote the use of innovative technologies that may achieve faster, less costly cleanups, EPA in 1996 agreed to share the risks associated with implementing innovative technologies for a limited number of approved projects by "underwriting" the use of certain promising innovative approaches. Under this risk-sharing program, EPA may agree to reimburse up to 50 percent of the cost of selected

innovative remedies if the remedy fails and subsequent remedial action is required.

EPA also learned that the lack of indemnification for prime contractors was hampering the use of innovative technology. Prime contractors are unwilling to recommend innovative technologies for fear that they will be sued for negligence if an innovative technology fails. Without indemnification, there is little incentive for the prime contractors to select an innovative technology. To address these concerns at Superfund projects, EPA expanded indemnification coverage to include both the prime contractor and the innovative technology contractor when indemnification is offered. Thus, both the technology vendor and the prime may be protected from third-party negligence claims resulting from a pollution release.

Tax and Other Financial Incentives. Government already provides financial incentives for the regulated community to clean up certain categories of contaminated sites. For example, the Internal Revenue Service (IRS) has ruled that certain costs incurred to assess and clean up soil and groundwater could be deducted as business expenses in the year incurred (rather than having to be capitalized over time). Expensing rather than capitalizing such costs (adding them to the basis for depreciation) can be a major benefit, depending on otherwise taxable income.

Recent revisions to the federal tax law provide even more incentive to motivate taxpayers to purchase, clean up, and redevelop brownfields (EPA, 1999b). The Brownfields Tax Incentive was passed as part of the Taxpayer Relief Act of 1997 to spur the cleanup and redevelopment of brownfields in distressed areas and to level the playing field between taxpayers who caused environmental contamination at certain properties and those who did not. Although criticized by the Government Accounting Office (GAO, 2000), the Brownfields Tax Incentive program may serve as a template for a similar program designed to incentivize DNAPL cleanups, where appropriate.

Another example of an economic incentive aimed at promoting innovative DNAPL remediation technologies is the concept of an “infeasibility fee” (National Research Council, 1994). This incentive would involve charging an annual fee to responsible parties for each site or operable unit issued a ARAR waiver due to technical impracticability. Funds could be used to encourage the use of aggressive DNAPL reduction technologies by reimbursing responsible parties for testing at their DNAPL sites. If the technology fails to achieve its intended goal and the responsible party is required to implement a contingency or backup technology, the responsible party would be able to recoup some or all of its losses from the infeasibility fee fund. If the innovative technology succeeded, then the fund would not subsidize the project.

5.3 Future ITRC Involvement in DNAPL Issues

The DNAPLs Team’s vision regarding the benefits of a DNAPL remediation strategy, combining source removal with intrinsic and enhanced natural plume attenuation, is to achieve acceptable and lasting DNAPL remediation with substantial overall savings of both time and money. This shared vision is the basis of the team’s discussions about overcoming obstacles to DNAPL source removal, both technical and regulatory, as part of a complete site remediation strategy.

5.3.1 Case Studies

The DNAPLs Team believes that more empirical evidence from full-scale field applications needs to be collected to verify the practicability and effectiveness of DNAPL mass removal. In 2001, the DNAPLs Team began to develop case summaries of sites where the technologies discussed in this document have been implemented to evaluate their cost and performance. We have developed draft case summaries on each of the following technologies: dynamic underground stripping/steam injection, six-phase heating, in situ thermal destruction, and in situ chemical flushing. As previously discussed, in situ chemical oxidation has been reviewed in more detail by another ITRC team. For this effort, performance will be measured by assessing the degree to which the DNAPL extraction technology removed or destroyed DNAPL mass in the subsurface. Ultimately, we would like to evaluate the technologies' performance based on their capacity to effect a significant improvement in groundwater quality.

5.3.2 Develop DNAPL Technical/Regulatory Guidance and Training Module

Documenting these deployments is a short-term goal of the DNAPLs Team. In the longer term, we feel that the issues brought up in this document need to be explored further. To this end, the DNAPLs Team has begun developing a series of technical/regulatory guidance documents based on the knowledge gained in developing the case summaries. To complement the planned technical/regulatory guidance document, the DNAPLs Team will also be developing a training module on DNAPL remediation technologies and related issues surrounding source zone remediation.

5.3.3 Contribute to Studies Assessing the Impact of Removing DNAPLs

While the long-term impacts of aggressive DNAPL source reduction are the subject of debate and can only be hypothesized at present, the potential rewards (e.g., improvements in groundwater quality and lower life-cycle costs) are worthy of pursuit. Studies should be designed to test the hypothesis, through cost-benefit analyses and long-term monitoring and modeling, that removing DNAPL source material does indeed result in a decrease in contaminant mass loading to the down gradient plume, shorter remedial time frames, and less overall cost. ITRC will support efforts to study this problem further, review technical reports from a regulatory perspective, and disseminate the results to state regulators and stakeholders. For example, EPA's Technology Innovation Office (TIO) is in the process of monitoring several sites where DNAPL remediation has or will take place to evaluate these issues, and ITRC is actively assisting.

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APPENDIX A

List of Acronyms

ACRONYMS

^{222}Rn	- Radon 222
^{238}U	- Uranium 238
3D	- three-dimensional format
AC	- alternate current
AFB	- Air Force Base
AFCEE	- Air Force Center for Environmental Excellence
ARA	- Applied Research Associates
ASTM	- American Society for Testing Materials
bgs	- below ground surface
BTEX	- benzene, toluene, ethylbenzene, xylene
cfm	- cubic feet per minute
CITT	- conservative interwell tracer test
CPEO	- Center for Public Environmental Oversight
CPT	- cone penetration test
CRREL	- Cold Regions Research and Engineering Laboratory
DCE	- dichloroethylene or dichloroethene
DNAPLs	- dense non-aqueous phase liquids
DO	- dissolved oxygen
DoD	- Department of Defense
DOE	- Department of Energy
DUS	- dynamic underground stripping
EIT	- electrical impedance tomography
EM	- electromagnetic
EMR	- electromagnetic resistivity survey
EOL	- electromagnetic offset logging
ERH	- electrical resistance heating
ERT	- electrical resistance tomography
Fe^{+2}	- ferrous iron, Iron II
ft	- feet or foot
GC	- gas chromatograph
GPR	- ground-penetrating radar
H_2O_2	- hydrogen peroxide
Hg	- Mercury
HPO	- hydrous pyrolysis/oxidation
IRP	- Installation Restoration Program
ISCO	- in situ chemical oxidation
ISCOR	- in situ chemical oxidation with recirculation
ITRC	- Interstate Technology and Regulatory Council
KMnO_4	- potassium permanganate
LNAPL	- light non-aqueous phase liquid
mm	- millimeter
MSDS	- Material Safety Data Sheet
MSL	- mean sea level
MTBE	- methyl tertiary butyl ether
NAPL	- non-aqueous phase liquid
O&M	- operation and maintenance

ACRONYMS (cont.)

OH\$	- hydroxyl radical
OST	- Office of Science and Technology
OU	- operable unit
PAH	- polynuclear aromatic hydrocarbon
PCBs	- polychlorinated biphenyls
PCE	- tetrachlorethylene <i>or</i> perchloroethene
PCP	- pentachlorophenol
PID	- photoionization detector
PITT	- partitioning interwell tracer test
ppm	- parts per million
PVC	- polyvinyl chloride
RDX	- royal demolition explosive or cyclonite
RHX	- halogenated organic compound
RNS	- Ribbon NAPL Sampler
ROI	- radius of influence
ROST	- Rapid Optical Screening Tool
SCAPS	- Site Characterization & Analysis Penetrometer System
SEAR	- Surfactant-Enhanced Aquifer Remediation
SPH	- Six-Phase Heating
SRS	- source removal system
SSLs	- soil screening levels
SVE	- soil vapor extraction
SwRI	- Southwestern Research Institute
TCA	- trichloroethane
TCE	- trichloroethene or trichloroethylene
TNT	- trinitrotoluene
TOC	- total organic carbon
TPH	- total petroleum hydrocarbon
TSWG	- Tribal and Stakeholder Working Group
VIP	- vertical induction profiling
VOA	- volatile organic analysis or analyte

APPENDIX B

Innovative DNAPL Characterization and Monitoring Tools Matrix

Innovative DNAPL Characterization and Monitoring Tools Matrix

Technology	Capabilities and Limitations	Data Quality	Data Usage
Geophysical Techniques			
Ground Penetrating Radar (GPR)	<ul style="list-style-type: none"> -Subsurface geologic features can be identified. -May determine most likely flow path of DNAPL. -Results can produce two-dimensional vertical profile. -Inability to directly detect DNAPL. -Inability to produce direct readings or measurements. -Highly dependent on soil moisture and soil type. 	<ul style="list-style-type: none"> -Highly qualitative and requires a high degree of subjective interpretation. -Should be calibrated with a core sample. 	<ul style="list-style-type: none"> -Define subsurface features. -Locate preferred DNAPL pathways (underground utilities). -Map shallow hydrogeologic interfaces.
Cross-Well Radar	<ul style="list-style-type: none"> -GPR principle applied down-hole. -Effective in saturated zone. -Can be applied down existing monitor wells. -Mostly limited to identifying plume sources. -Distance between monitor wells controls effectiveness. 	<ul style="list-style-type: none"> -Gross characterization technology that requires lab sample confirmation 	<ul style="list-style-type: none"> -Characterize high concentration of DNAPL. -Data should be used in conjunction with dielectric logging.
Electrical Resistance Tomography	<ul style="list-style-type: none"> -Measures electrical resistivity between boreholes. -Based on resistively contrast between soil/groundwater contamination and indigenous material. -Dependent on soil type, degree of saturation, geology. -Results can produce three-dimensional geologic profile. -Possible interference from steel monitor wells, pipelines, or underground utilities. 	<ul style="list-style-type: none"> -Highly qualitative and requires a high degree of subjective interpretation. -Should be calibrated with a core sample. 	<ul style="list-style-type: none"> -Characterize high concentration of DNAPL. -Map shallow hydrogeologic interfaces.
Vertical Inductive Profiling	<ul style="list-style-type: none"> -Surface to borehole configuration can measure the resistivity contrast between DNAPL and groundwater. -Can produce three-dimensional profile of lateral and vertical configuration of contamination. -Effective in PVC-cased or open holes only. 	<ul style="list-style-type: none"> -Highly qualitative and requires a high degree of subjective interpretation. -Should be calibrated with a core sample. 	<ul style="list-style-type: none"> -Characterize high concentration of DNAPL -Map shallow hydrogeologic interfaces
High Resolution 3-D Seismic Reflection	<ul style="list-style-type: none"> -Produces acoustical waves that detect subsurface density changes. -Provides three-dimensional map of subsurface features. -Not specific for DNAPL detection. 	<ul style="list-style-type: none"> -Requires background information on site conditions for proper interpretation of data. 	<ul style="list-style-type: none"> -Define subsurface anomalies and boundaries

Innovative DNAPL Characterization and Monitoring Tools Matrix

Technology	Capabilities and Limitations	Data Quality	Data Usage
<p>High Resolution Electromagnetic Resistivity Survey</p>	<ul style="list-style-type: none"> -Surface to borehole configuration. -Produce surveys capable of identifying high resistivity anomalies representative of DNAPL. -Tunable transmitter and receiver can overcome deployment barriers and electrical noise. -Does not specifically detect DNAPLs. 	<ul style="list-style-type: none"> -Gross characterization technology that requires lab sample confirmation. -Detection of fractures and channels that serve as preferred DNAPL pathways. 	<ul style="list-style-type: none"> -Define subsurface anomalies and boundaries
Intrusive Site Characterization Techniques			
<p>Cone Penetrometer (CPT) coupled with induced laser fluorescence</p>	<ul style="list-style-type: none"> -Useful when deployed with sampling devices and sensors. -Can provide continuous real time data on soil stratigraphy and contaminant distribution. -Relatively quick, cost-effective, minimally invasive. -Limited by surface features and extreme subsurface conditions (bedrock, boulders, and tight clays). 	<ul style="list-style-type: none"> -Qualitative screening for the presence of NAPLs. -Typically requires calibration with geologic borehole data for accurate interpretation of stratigraphy. 	<ul style="list-style-type: none"> -Delineation of stratigraphy and identification of potential preferential pathways. -Delineation of gross contamination and NAPL
<p>Direct Push Membrane Interface Probe (MIP)</p>	<ul style="list-style-type: none"> -Can provide continuous real time data on contaminant distribution. -Can be coupled with CPT to compare stratigraphy to contaminant distribution. -Cannot detect contaminants at low concentrations. -Limited by surface features and extreme subsurface conditions (bedrock, boulders, and tight clays). 	<ul style="list-style-type: none"> -Qualitative to quantitative screening of contamination 	<ul style="list-style-type: none"> -Delineation of gross contamination, source identification
<p>Direct Push Discrete Interval Groundwater Sampling</p>	<ul style="list-style-type: none"> -Can provide continuous real time data on contaminant distribution. -Limited by surface features and extreme subsurface conditions (bedrock, boulders, and tight clays). 	<ul style="list-style-type: none"> -Quantitative screening of contamination. 	<ul style="list-style-type: none"> -Delineation of contamination and DNAPL source identification

Innovative DNAPL Characterization and Monitoring Tools Matrix

Technology	Capabilities and Limitations	Data Quality	Data Usage
Other DNAPL Site Characterization Techniques			
Ribbon NAPL Sampler	<ul style="list-style-type: none"> -Continuous direct sampling device applied down boreholes. -Provides detailed depth discrete mapping of NAPLs. -Sampling membrane must be in contact with NAPL. -Effective for pure phase hydrophobic contaminants only. 	-Colorimetric qualitative screening.	-Positive / negative indicator for the presence of NAPL.
Partitioning Interwell Tracer Test (PITT)	<ul style="list-style-type: none"> -Injection and monitoring of tracers in contaminant zone used to measure the volume of DNAPL. -Based on large-scale application of chromatography. -Injection of tracers may have regulatory implications. -Not appropriate for quantifying free phase DNAPL. -Quantitative for residual DNAPL in the targeted zone. 	<ul style="list-style-type: none"> -Quantify and locate residual DNAPL contamination. -Allows detailed planning for remediation. 	<ul style="list-style-type: none"> -Used to estimate residual saturation and DNAPL source mass. -Used primarily in conjunction with chemical flushing technologies.

APPENDIX C

Innovative DNAPL Source Remediation Technologies Matrix

Innovative DNAPL Source Remediation Technologies Matrix

Technology	Description/Definition	Applicability/Limitations	Example Projects
In Situ Thermal Technologies			
Steam Enhanced Extraction (SEE)	<ul style="list-style-type: none"> -Combination of steam injection and vacuum extraction -Enhancement of soil vapor extraction (SVE) and groundwater extraction process -Injection typically run in pulsed-mode with continuous vacuum extraction following steam breakthrough -Convective heating process 	<ul style="list-style-type: none"> -Applicable to recovery of organic compounds from both saturated and vadose zones -Most effective in coarse-grained lithologies -Limited applicability in silt or clay -May enhance biodegradation processes 	<ul style="list-style-type: none"> -LLNL Gas Pad, CA -Visalia Pole Yard, CA -Alameda Point Site 5, CA -Portsmouth GDP, OH -Savannah River A/M Area, SC -Cape Canaveral LC-34, FL
Electrical Resistance Heating (ERH)	<ul style="list-style-type: none"> -Uses application of 3- or 6-phase electrical power and resistivity of soil particles to heat subsurface -Delivered to the subsurface by buried electrodes -Electrical current flows from each electrode to adjacent out-of-phase electrodes -Results in generation of steam -Not dependent on fluid transfer like steam technologies 	<ul style="list-style-type: none"> -Applicable to low-permeability zones (silt and clay) since these layers are heated preferentially -May enhance biodegradation processes 	<ul style="list-style-type: none"> -ICN Pharmaceuticals, OR -Cape Canaveral LC-34, FL -Paducah GDP, KY -Charleston Naval Complex, SC -Skokie, IL -Fort Richardson, AK
Dynamic Underground Stripping (DUS)	<ul style="list-style-type: none"> -Simultaneous injection of steam and electrical energy combined with vacuum extraction -Steam injected into permeable strata -Electrical energy applied to less permeable strata 	<ul style="list-style-type: none"> -Applicable to treatment of organic compounds in both saturated and vadose zones -Effective in coarse- and fine-grained lithologies -May enhance biodegradation processes 	<ul style="list-style-type: none"> -LLNL Gas Pad, CA -Pinellas STAR Center, FL (future) -Visalia Pole Yard, CA -Savannah River A/M Area, SC
Hydroxyl Pyrolysis Oxidation (HPO)	<ul style="list-style-type: none"> -Chemical oxidation process that occurs in the dissolved phase at elevated soil temperatures -Destroys contaminants in place -Oxidation reactions enhanced by the injection of air/oxygen with steam and cycling pressure to optimize mixing 	<ul style="list-style-type: none"> -Mechanisms not understood completely -Requires co-injection of air/oxygen -Most effective at deep sites where higher pressures and temperatures are achieved -Limited applicability at shallow unconfined aquifer sites where VOCs may vaporize out of solution faster than reacting 	<ul style="list-style-type: none"> -Visalia Pole Yard, CA -Savannah River A/M Area, SC -Beale AFB, CA (future)
Thermal Conduction Heating	<ul style="list-style-type: none"> -Applies heat to the soil by a combination of thermal conduction and vacuum -Heats soil to temperatures above boiling point of water -Not dependent on permeability of soil -Destroys 95% of contaminant mass in the ground -Configured for treatment of surface (thermal blankets) or subsurface soil (thermal wells) 	<ul style="list-style-type: none"> -Applicable to high boiling point contaminants, like PCBs, PAHs, pesticides, and heavy hydrocarbons -Limited to unsaturated zone since influx of water may preclude complete vaporization -May require extensive dewatering or hydraulic control if applied below water table 	<ul style="list-style-type: none"> -Missouri Electric Works, MO -Centerville Beach, CA -Portland, IN -Naval Facility Ferndale, CA -Rocky Mtn Arsenal, CO (future) -Alhambra Pole Yard, CA (future)

Innovative DNAPL Source Remediation Technologies Matrix

Technology	Description/Definition	Applicability/Limitations	Example Projects
Surfactant Enhanced Aquifer Remediation (SEAR)	<ul style="list-style-type: none"> -Involves the injection and extraction of surfactant solution to solubilize and/or mobilize DNAPLs -Solubilized DNAPL travels within microemulsions that are readily transported through the aquifer -Includes hydraulic control to direct flow of injectate and prevent uncontrolled DNAPL migration -Extracted fluids are treated above ground to separate contaminants from the surfactant waste stream -Surfactant flood followed by water flood 	<ul style="list-style-type: none"> -Applicable to treatment of volatile and semi-volatile compounds in saturated zone -May be suitable for treatment beneath structures that are inaccessible using other technologies -Recovery and recycling of surfactant may be necessary to be cost-effective at large sites -The DNAPL zone must be carefully characterized prior to SEAR activities in order to develop a cost-effective SEAR design -Low-permeability zones may not be treated effectively 	<ul style="list-style-type: none"> -Hill AFB OU2, UT -Camp Lejeune Site 88, NC -NAS Alameda, CA -Dover AFB, DE -Alameda Point Site 5, CA
Co-Solvent Flooding	<ul style="list-style-type: none"> -Involves the injection and extraction of cosolvents, such as alcohol to solubilize and/or mobilize DNAPLs -Reduces interfacial tension of DNAPL -Similar to SEAR in design/implementation 	<ul style="list-style-type: none"> -Applicable to treatment of volatile and semi-volatile compounds in saturated zone -Alcohol cosolvent may act as substrate to enhance anaerobic biodegradation 	<ul style="list-style-type: none"> -Sage's Drycleaner, FL -Hill AFB OU1, UT
Enhanced Desorption and Bioremediation			
Enhanced Reductive Dechlorination	<ul style="list-style-type: none"> -Involves injection of organic substrate into subsurface, which releases hydrogen (electron donor) upon fermentation -Applied by direct-push injection or backfill-auguring -Commercial electron donors include sodium lactate, Hydrogen Release Compound (HRC), molasses, methanol, vegetable oil -Enhances reductive bioattenuation process in dissolved phase -Facilitates desorption of sorbed material via development of steep concentration gradient and release of biosurfactants 	<ul style="list-style-type: none"> -Applicable to hydrophobically sorbed contaminant and dissolved-phase contaminants -May be applicable to moderate levels of residual DNAPL -May not be cost-effective in highly aerobic zones 	<ul style="list-style-type: none"> -Springdale Cleaners, OR -INEEL Test Area North, ID

Innovative DNAPL Source Remediation Technologies Matrix

Technology	Description/Definition	Applicability/Limitations	Example Projects
In Situ Chemical Oxidation Technologies			
Hydrogen Peroxide (Fenton's Reagent)	<ul style="list-style-type: none"> -Involves injecting hydrogen peroxide and iron catalysts into subsurface -Reaction forms hydroxyl radicals -Delivery methods include soil mixing, direct injection, and oxidant recirculation -Results in oxidation of organic contaminants 	<ul style="list-style-type: none"> -Applicable to wide range of organics -Fenton's reaction requires low pH conditions and may not be effective at high alkalinity sites -Subsurface heterogeneities can cause nonuniform distribution of oxidant -Limited by mass transfer limitations and/or poor contact due to displacement of the contaminant during reagent injection -May need more than one application of oxidant to remediate rebound effects -Native organic matter exerts a demand for oxidants, thus increasing costs for chemicals 	<ul style="list-style-type: none"> -NSB Kings Bay, GA -NAS Pensacola, FL
Permanganate (potassium or sodium)	<ul style="list-style-type: none"> -Involves injecting permanganate into subsurface -Delivery methods include soil mixing, direct injection, and oxidant recirculation -Results in direct oxidation of organic contaminants 	<ul style="list-style-type: none"> -Subsurface heterogeneities can cause nonuniform distribution of oxidant -Limited by mass transfer limitations and/or poor contact due to displacement of the contaminant during reagent injection -Not affected by pH -May cause increase in dissolved manganese levels -Effective porosity of the subsurface may be reduced due to precipitation of manganese oxides -May need more than one application of oxidant to remediate rebound effects 	<ul style="list-style-type: none"> -Cape Canaveral LC-34, FL -Butler Cleaners, FL

APPENDIX D

**DNAPLs Team Contacts, ITRC Fact Sheet, ITRC Product List, and
Document Evaluation Survey**

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