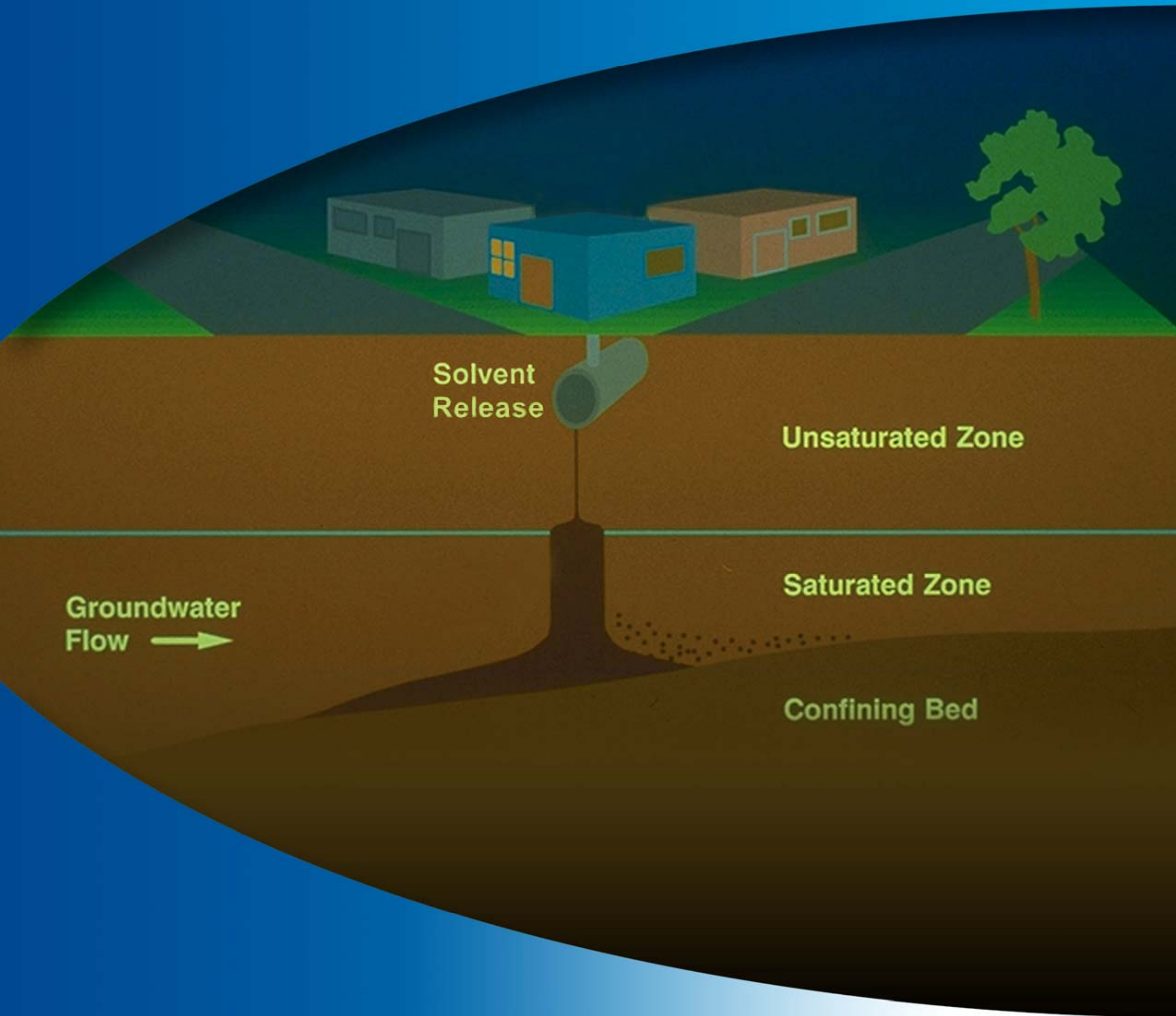
DNAPL Management Overview



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14. ABSTRACT
This Dense Non-aqueous Phase Liquid (DNAPL) Management Overview provides an introduction on how to manage DNAPL contamination at a site. Because DNAPL sites can be very challenging, this document focuses heavily on the limitations of characterizing and removing DNAPL, and how to make realistic management decisions in the midst of these uncertainties. Part of the challenge is that no technology has consistently achieved maximum contaminant levels (MCLs) at DNAPL sites; in fact, to date there are no documented, peer-reviewed case studies where MCLs were achieved throughout the DNAPL source zone. Another part of the challenge is that applying source-zone remediation technologies without well-defined project objectives will likely lead to excessive costs, risks, or failures. Two case studies are presented to highlight different approaches to managing sites impacted with DNAPL. The information provided in this Overview is based on Navy Remediation Innovative Technology Seminar (RITS) presentations given in October 2001 and Spring 2006.

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Introduction

This Dense Non-aqueous Phase Liquid (DNAPL) Management Overview provides an introduction on how to manage DNAPL contamination at a site. Because DNAPL sites can be very challenging, this document focuses heavily on the limitations of characterizing and removing DNAPL, and how to make realistic management decisions in the midst of these uncertainties. Part of the challenge is that no technology has consistently achieved maximum contaminant levels (MCLs) at DNAPL sites; in fact, to date there are no documented, peer-reviewed case studies where MCLs were achieved throughout the DNAPL source zone. Another part of the challenge is that applying source-zone remediation technologies without well-defined project objectives will likely lead to excessive costs, risks, or failures. Two case studies are presented to highlight different approaches to managing sites impacted with DNAPL. The information provided in this Overview is based on Navy Remediation Innovative Technology Seminar (RITS) presentations given in October 2001 and Spring 2006.

What is DNAPL?

DNAPLs are liquids that do not readily dissolve in water. Because they have densities greater than water, they typically sink in groundwater. Chlorinated solvents, such as trichloroethylene, and PCBs are common DNAPLs. There are two forms of DNAPL: free-phase (mobile) and residual. **<u>Free-phase (mobile)</u>** DNAPL is under positive pressure and can potentially drain to a well-placed monitoring well or be removed using extraction wells. **<u>Residual</u>** DNAPL is held under capillary pressure, meaning that the DNAPL will remain immobile unless replenished by new releases or subjected to an applied force sufficient to overcome the capillary pressure.

Where is the DNAPL?

DNAPLs in the subsurface are typically the result of surface spills or disposal. The DNAPLs flow downward within the subsurface via gravity along a permeable pathway, potentially spreading laterally or changing directions as less permeable material is encountered. DNAPL can move via gravity upgradient of the general groundwater flow direction if the lithology angles in that direction. The DNAPL may accumulate or "**<u>pool</u>**" on top of less permeable layers, as illustrated on Figure 1. The resulting DNAPL pools may be very thin. Residual DNAPL remains smeared along the pathway, both within the vadose and saturated zones. Because the pathway that the DNAPL follows depends on the unique heterogeneities of the site, it may be difficult to know where the DNAPL ends up.

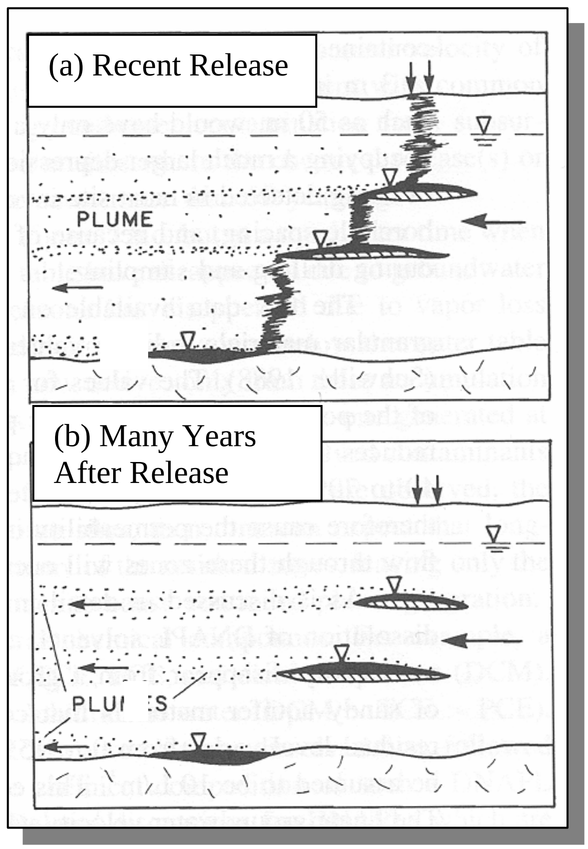

Figure 1: Typical DNAPL Distribution at Two Different Times (Modified from Pankow and Cherry, 1996).

How do DNAPLs impact groundwater?

Over time, typically over a period of decades, the DNAPL gradually dissolves into groundwater. The rate of dissolution is very slow due to low aqueous solubility, slow movement of groundwater, and the small surface area of DNAPL relative to contaminant mass. Figure 1 illustrates how some residual DNAPL, present after a release at time (a), has dissolved after many years (b), while some of the DNAPL with less surface area exposed to flowing groundwater remains in place. This “residual DNAPL does not migrate. Figure 1 also illustrates how the dissolved concentrations in groundwater are impacted by the location of the residual DNAPL. In practice, it is difficult to characterize groundwater concentrations with sufficient precision to assist with identifying the location of DNAPL.

Figure 2 illustrates, on a microscopic level, how DNAPL distributions change with time, again referring to timeframes covering years or decades. The circles represent a detail of DNAPL distribution within a rock fracture at three different times: (a) at an early time after a release occurs, the DNAPL is interconnected meaning that the DNAPL is continuous between different fractures or pore spaces; (b) at an intermediate time, some of the DNAPL has dissolved, leaving isolated DNAPL “blobs;” and (c) at a *much* later time, the DNAPL has fully dissolved into groundwater. While the figure illustrates DNAPL diffusion within fractured rock, this micro-scale view of DNAPL distribution applies within any number of formations. In addition, the fact that disconnected DNAPL blobs may be characteristic of an older DNAPL plume complicates DNAPL characterization and removal, as the disconnected DNAPL blobs are much more difficult to locate within the subsurface.

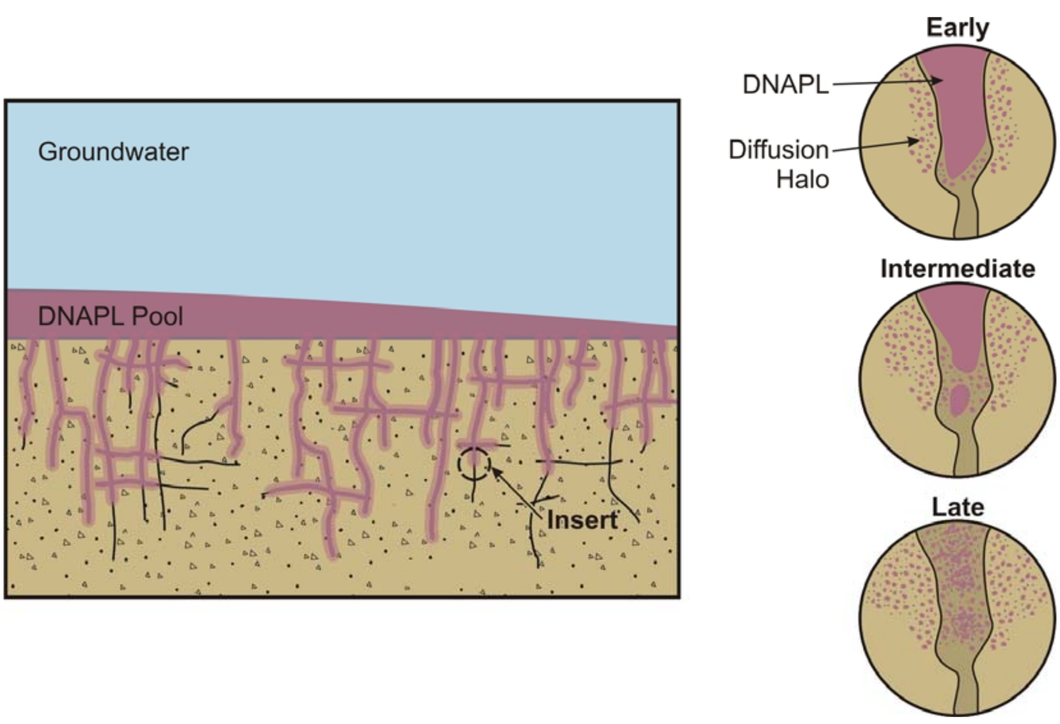

Figure 2: DNAPL Diffusion through Fractured Media with Time (Modified from Pankow and Cherry, 1996).

The **DNAPL source zone** is defined as the area which has been in contact with DNAPL, and can include (1) residual DNAPL, (2) pooled (free-phase) DNAPL, (3) contaminants sorbed to soil, and (4) dissolved contaminants diffused through fine-grained media. The DNAPL zone acts as a long-term, continuing source to the downgradient dissolved aqueous plume. The **plume** is the contaminated groundwater emanating from the source. See Figure 3 for a depiction of the DNAPL source zone and plume. In actuality, distinguishing the source and plume is not always easy.

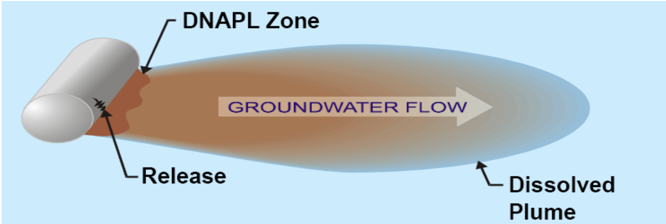

Figure 3: DNAPL Distribution

What are the difficulties associated with DNAPL characterization?

Before DNAPL source remediation can be evaluated and effectively applied, site characterization data must be gathered, not just with respect to site lithology and hydrogeology, but also with respect to:

1. DNAPL characteristics
    - Distribution through geology
    - Mass
    - Age
    - Density, viscosity, composition
2. Aqueous plume characteristics
    - Extent
    - Stable or expanding?

Obtaining adequate site characterization data can be very challenging, particularly if the DNAPL cannot be located. Furthermore, even if DNAPL is located, "determining the actual mass and spatial distribution of the DNAPL mass is very difficult" (U.S. EPA, 2003) and is generally not accurate. Insufficient site characterization data contributes to ineffective application of remediation technologies.

This document does not focus on methodologies of characterization. For more information about specific characterization technologies and tools available, review the RITS 2003 presentation titled "DNAPL Detection and Characterization Techniques" (https://portal.navfac.navy.mil/pls/portal/docs/PAGE/NAVFAC/NAVFAC_WW_PP/NAVFAC_NFESC_PP/ENVIRONMENTAL/ERB/RITS_PAGE/TAB5390723/2003-04-DNAPL.PDF).

DNAPL characterization tools have advanced in recent years, but direct observation of DNAPL is still difficult. Even when DNAPL is detected, it is expensive and nearly impossible to identify the pathways and extent of the DNAPL. Furthermore, characterization uncertainties and requirements increase at sites with subsurface complexity, and at sites with large and multiple source zones. In practice, DNAPL sites are very difficult to characterize, and DNAPL zones can only be defined in general terms.

These site characterization difficulties have led to methods to indirectly infer or predict the presence of DNAPL through dissolved phase concentrations and distribution, as discussed in the following section.

How can the presence of DNAPL be predicted?

Dissolved phase aqueous concentrations may be used to predict the presence of DNAPL. Although lab experiments show NAPL: water equilibrium at 10-100 centimeters per day (cm/d) flow, groundwater concentrations at DNAPL sites are typically between 1% and 10% of solubility due to non-uniform NAPL distribution, mixing of groundwater in wells, and effective solubility. For example, groundwater TCE concentrations of 55 ppm at 5% of solubility (1,100 ppm for TCE) would indicate that DNAPL is likely present.

Complex DNAPL distribution may lead to highly stratified dissolved plume concentrations, as illustrated in Figure 1. For example, vertical concentration profiles within the groundwater can identify depths with higher concentrations, which may coincide with zones containing DNAPL and be used to predict the presence of DNAPL.

Other indirect evidence of DNAPL includes dissolved concentrations increasing with depth without another explanation, PVC well softening, swelling, failure, concentrations increasing up hydraulic gradient from a release area, tailing and rebound, and organic vapor analysis exceeding 100-1,000 parts per million by volume (ppmv).

Can Mass Flux be used to assess DNAPL impact to groundwater?

The evaluation of downgradient contaminant mass flux distribution is increasingly being attempted during characterization to assess DNAPL impact to groundwater. The calculation of mass of dissolved contaminants per unit cross-sectional area provides an estimate of DNAPL source strength and mass loading. Eventually, it may become the metric for assessing source remediation, as opposed to other metrics such as MCLs that are generally unattainable for DNAPL.

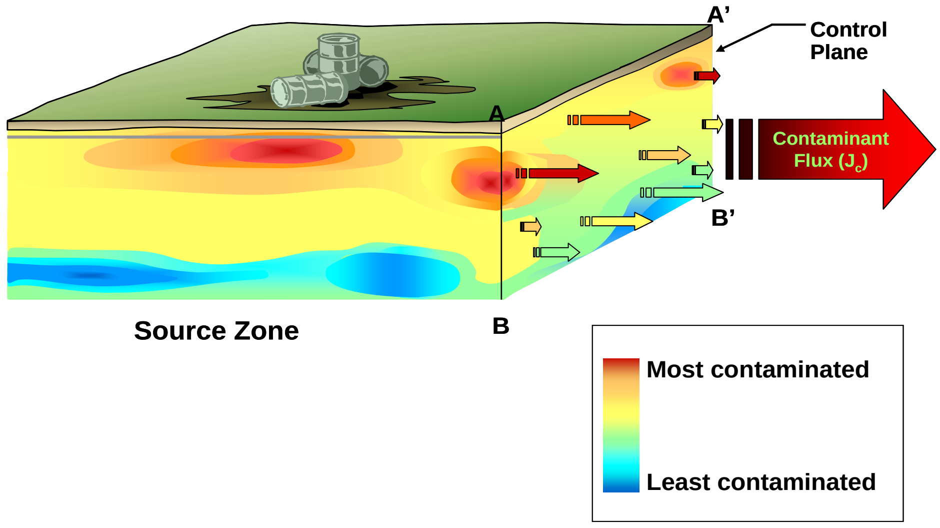

Figure 4: Mass Flux away from DNAPL (Enfield, 2001).

There are several methods that have been proposed for measuring mass flux, but each has limited testing and their relative accuracies have yet to be determined. The three most common methods are:

1. Using water quality data from transects (multiple locations and depths) and groundwater velocity.
2. Using downgradient aquifer tests in a transect of wells (Bockelman et al.; Ptak and Teutsch, 2000).
3. Using sorptive permeable media in downgradient wells to intercept contaminated groundwater and release resident tracers (Hatfield et al., 2001).

It is not yet certain how mass flux can help a site move toward closure. Regulations do not yet address mass flux, and do not yet specify what amount of mass flux is acceptable. Remedial project managers planning to use reduction of mass flux as a remedial or performance objective should implement a rigorous data quality objective (DQO) evaluation process to specify precisely how mass flux data will be utilized to make management decisions.

What are the basic DNAPL management options?

If DNAPL is suspected but not fully characterized, the project manager has basically three options:

1) Continue spending money on site characterization.
2) Proceed with source zone remediation.
3) Focus on containing the resulting dissolved-phase plume, and request a Technical Impracticability (TI) waiver if necessary.

As noted in previous sections, DNAPL is very difficult to characterize, and further characterization may not achieve the level of knowledge necessary to successfully implement source zone treatment. Without correct and sufficient knowledge, implementing an effective source zone treatment technology is practically impossible. With this in mind, available treatment technologies and approaches are summarized in the following sections, along with their benefits and limitations.

What technologies are available for DNAPL management?

A number of technologies have been applied at DNAPL remediation sites, but their success is often directly proportional to the quality of the site characterization data. Some remedial technologies focus on the aqueous plume, some on the DNAPL source zone, and some use a combination of technologies. Many of these technologies have been discussed in previous RITS presentations (see Environmental Restoration & BRAC [ERB] website, past RITS), as noted below by year.

Aqueous plume technologies:

- Monitored natural attenuation (MNA) (RITS 2001, 2003)
- Pump and treat
- Permeable reactive barrier (RITS 1998, 2002, 2005)
- Enhanced biodegradation (RITS 2000)
- Well-head treatment

DNAPL source technologies:

- Containment (physical, hydraulic, or MNA [see above])
- Mass destruction (chemical oxidation [RITS 2000, 2003], thermal [RITS 2000, 2006])
- Mass removal (excavation; surfactant flushing [RITS 1998, 2006])

Combined:

- Treatment trains: removing source mass and treating aqueous plume (RITS April 2005)

Case Study 1 in Appendix A illustrates chemical oxidation as a remedial strategy. Case Study 2 in Appendix B describes physical and hydraulic containment and in situ biological groundwater treatment.

What are the limitations of source removal technologies?

The biggest limitation is that no DNAPL remediation technology will likely achieve MCLs. After two decades of application of DNAPL source removal technologies, the following observations can be made:

- Many DNAPL source removal technologies are still under development with further research needs being identified.
- Many source zone removal technologies have only been tested on a pilot scale, and have not proceeded to full-scale application.
- For technologies that have been more extensively tested, the success of mass removal and destruction is difficult to assess because the initial mass is often unknown and may be overestimated using best-case assumptions.
- Only partial DNAPL mass removal or destruction can be achieved (see study results summarized in Figure 5)

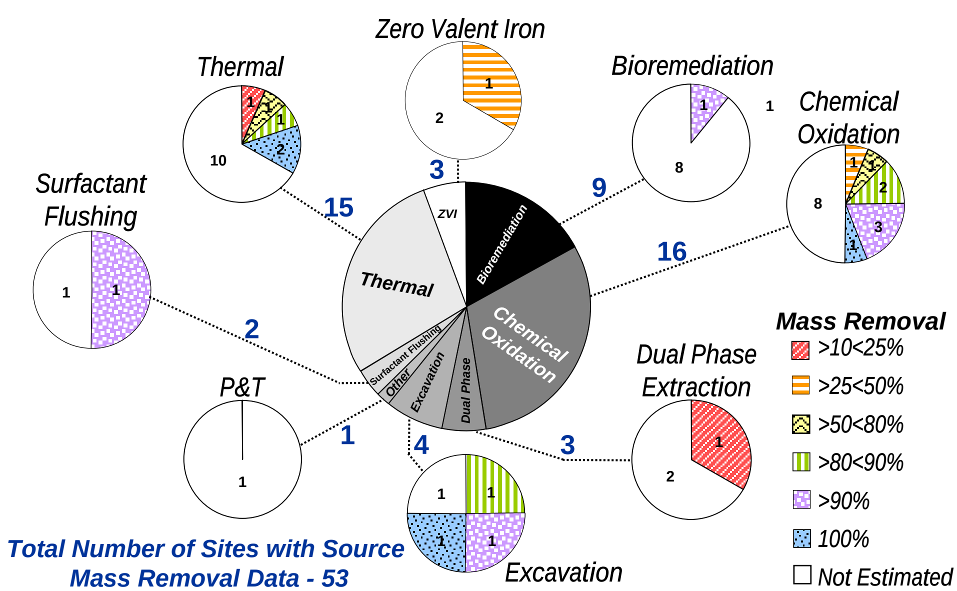

Figure 5. Summary of Source Mass Removal Sorted by Technology (GeoSyntec & Lebron, 2004)

- Mass removal generally causes only a limited reduction in mass flux (see study results summarized in Figure 6).
- State and federal MCLs are extremely unlikely to be met.
- DNAPL treatment risks include the potential to mobilize DNAPL, create unfavorable changes to the DNAPL distribution, or negatively impact the microbiology and natural attenuation that may already be occurring.

In summary, applying the available technologies without well-defined project objectives will likely lead to excessive costs, risks, or failures.

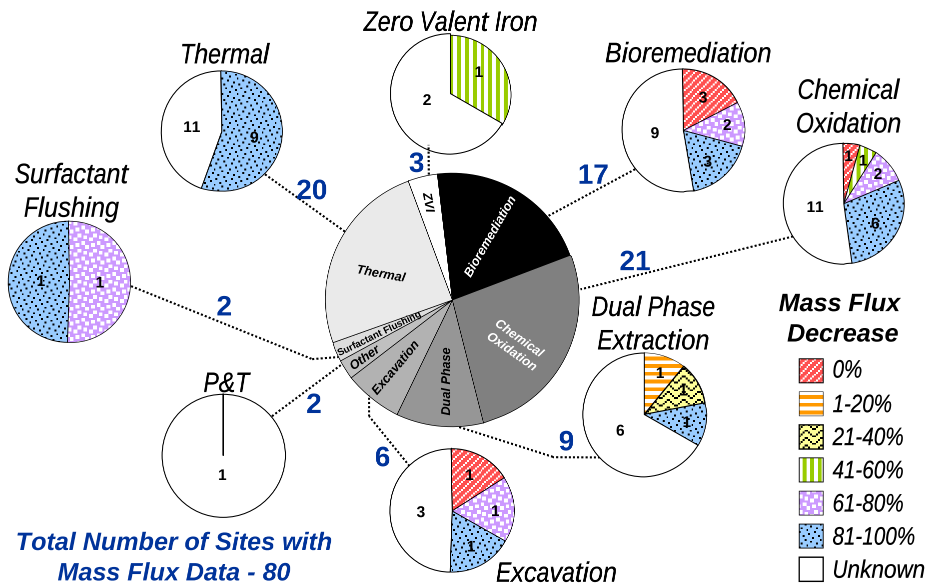

Figure 6. Summary of Mass Flux Decrease Sorted by Technology (GeoSyntec & Lebron, 2004)

Are DNAPL remediation expectations too high?

The overall goal for cleaning up groundwater affected by a DNAPL release is to protect human health and the environment. However, meeting state and federal MCLs appears not to be feasible in DNAPL remediation, even when the DNAPL scenario is "ideal". To date, there are no documented, peer-reviewed case studies where MCLs were achieved throughout the DNAPL source zone. At least one DNAPL site has obtained closure through DNAPL source reduction, but MCLs were not achieved throughout the DNAPL treatment area (ITRC, 2004). Reduction of downgradient mass flux could be a quantitative goal, but to date this has not been regulated and the benefits of using it as a metric are uncertain.

For small, shallow sources in permeable media, mass removal (possibly via excavation) and/or destruction may be the preferred remedies. See Appendix A for a case study involving a small, shallow DNAPL source in permeable media. For large sources, especially in low permeability and/or heterogeneous media and/or in deep formations, mass removal is unlikely to reduce risks sufficiently to allow site closure or response complete. Therefore, a **risk management** approach, possibly focusing on source zone containment, may be the only viable option available for large source zones. See Appendix B for a case study involving a large source which primarily used containment as the remediation technology. Projects with large source zones may require a Technical Impracticability (TI) waiver, though historically these have been difficult to obtain and therefore few sites have obtained them. A TI waiver is one of six types of ARAR waivers defined in CERCLA and the National Contingency Plan (NCP), where "compliance with the requirement is technically impracticable from an engineering perspective."

What are the potential benefits of DNAPL mass reduction?

Potential benefits of DNAPL mass reduction include:

- Reduced DNAPL mobility
- Reduced mass flux from source zone
- Increased reliability of long-term containment
- Reduced time of remediation and costs
- Reduced environmental risk

Ideally, partial DNAPL mass removal results in a decrease in mass flux from the source zone resulting in a stable or shrinking aqueous plume due to natural attenuation. This ideal scenario is depicted in Figure 7. However, as noted earlier, the mass reduction is rarely sufficient to allow Site Closeout or Response Complete, particularly if the remedial action objectives are based on MCLs rather than risk reduction.

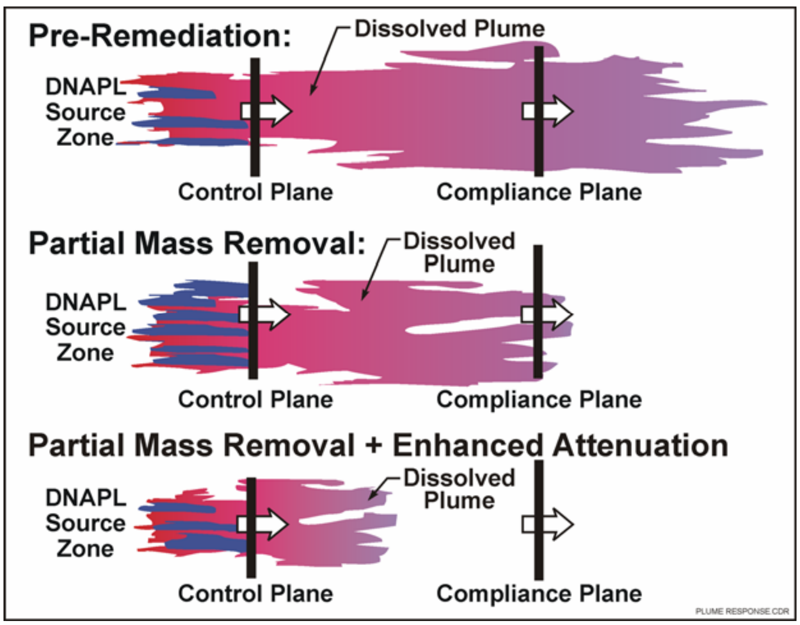

Figure 7: Ideal Changes in DNAPL with Mass Removal (USEPA, 2003).

What are the potential negative impacts of DNAPL mass reduction?

Potential negative impacts of DNAPL mass reduction include:

- Expansion of the DNAPL source zone due to mobilization of residual DNAPL
- Undesirable changes in the DNAPL distribution
- Undesirable changes in physical, geochemical, and microbial conditions
- Adverse impact on subsequent remediation technologies
- Increased life-cycle costs of site cleanup

Is partial mass removal a viable option?

Achieving partial mass removal from the DNAPL source area may decrease the downgradient mass flux, but the metrics to measure it are uncertain. Several models have been developed to predict the impact of mass removal (Sale and McWhorter, 2001; Rao & Jawitz, 2003). However, these models have limitations, including (1) they do not predict how much mass will be removed; (2) model predictions will vary depending on the assumed conditions; (3) they have limited field verification.

The long-term benefit and economic value of partial mass removal is difficult to predict. A mass flux reduction will not likely result in a satisfactory concentration reduction desired to meet remedial action objectives (usually MCLs). For example, with the Rao-Jawitz model, a 90% mass reduction yields a normalized concentration two or more orders of magnitude above the typical target cleanup level. Downgradient aqueous plume treatment and/or containment will likely be required in spite of significant mass removal. Only under an ideal scenario (e.g., small recent DNAPL spill at a shallow homogeneous site), will mass removal result in a sufficient decrease in mass flux from the source zone to allow MNA to achieve a stable or shrinking aqueous plume.

Partial mass removal may reduce risks to human health and the environment by "mitigating the future potential for human contact and exposure through long-term reduction of volume, toxicity, and mobility of the DNAPL" (U.S. EPA, 2003). In reality, it is difficult to remove sufficient mass to significantly reduce the actual risk. Moreover, if the remedial objective is to reach MCLs, that objective will unlikely be met. In either case, downgradient aqueous plume treatment and/or containment will likely be required in conjunction with the source removal if implemented.

DNAPL Management Considerations and Strategy

The Navy remedial project manager (RPM) and contractors should take into account the characterization and technology limitations discussed in this document and evaluate how best to manage site DNAPL. First, the project manager will need to determine potential risks of:

- Continued DNAPL migration
- Vapor transport and potential exposure
- Impacts to water supply wells
- Discharge to surface water
- Direct contact or ingestion

After characterizing the site risks, the project manager will then need to ask several important questions, including:

- Is the plume naturally attenuating? If so, is MNA alone appropriate?
- Is an aqueous plume remedial technology alone appropriate?
- Will partial mass removal change the need for plume containment?
- Have sufficient pilot studies been conducted at other sites to draw conclusions regarding effectiveness of remedial technologies at the site?
- Containment versus mass removal – both will reduce mass flux, so which can be implemented most cost-effectively?
- Do potential benefits of mass reduction justify the additional costs and risks?
- Are remedial action objectives attainable?

Project managers should remember these key points:

- Use knowledge, cost and performance reports, and case studies from other similar sites to help determine a cost-effective management strategy that will meet remedial action objectives.
- For small, shallow sources in permeable media, cleanup (mass removal and/or destruction) is the preferred remedy, with excavation likely the most effective solution.
- For large sources, especially in low permeability and/or heterogeneous media and/or in deeper formations, mass removal is unlikely to reduce risks sufficiently to allow Site Closeout or Response Complete.
- For these large sources, various risk management strategies should be considered, including source containment or plume treatment.

Also remember these key points to manage expectations of stakeholders:

- Research projects that involve multiple source zone applications and subsequent aqueous plume treatment (treatment trains) are difficult to specify *a priori* in a regulatory cleanup agreement – there is too much uncertainty regarding the potential effectiveness and results.
- At this time, it is difficult to predict how well a mass removal remedy will remove mass and reduce the downgradient mass flux – predictive models contain a great deal of uncertainty.
- Mass flux reduction is not a regulatory requirement, but can be a useful tool.
- Mass flux can be reduced by either mass removal or containment (and neither is generally perfect).

Where can you obtain additional guidance?

Interstate Technology and Regulatory Council (ITRC) DNAPL documents:
http://www.itrcweb.org/gd_DNAPLs.asp

NAVFAC Environmental Restoration and BRAC (ERB) website:
https://portal.navfac.navy.mil/portal/page?_pageid=181,5346904&_dad=portal&_schema=PORTAL#slide2_start

U.S. EPA links to DNAPL characterization and remediation:
http://www.cluin.org/issues/default.focus/sec/Dense_Nonaqueous_Phase_Liquids_(DNAPLs)/cat/Overview/

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Remediation Innovative Technology Seminar (RITS) presentations can be found at the NAVFAC website: http://enviro.nfesc.navy.mil/scripts/WebObjects.exe/erbweb.woa#slide_show_end

Appendix A: Case Study I—Example of Mass Removal at a Small, Shallow PCE Source in Permeable Media

Site Description:

At Naval Submarine Base (NSB) Kings Bay, Georgia, an abandoned municipal landfill used from 1974-1981 left multiple small, tetrachloroethylene (PCE) DNAPL source zones. The source zones were identified with field gas chromatography. The DNAPLs were situated in a fine sandy media with silt beds. The site is characterized by a high rate of natural biodegradation.

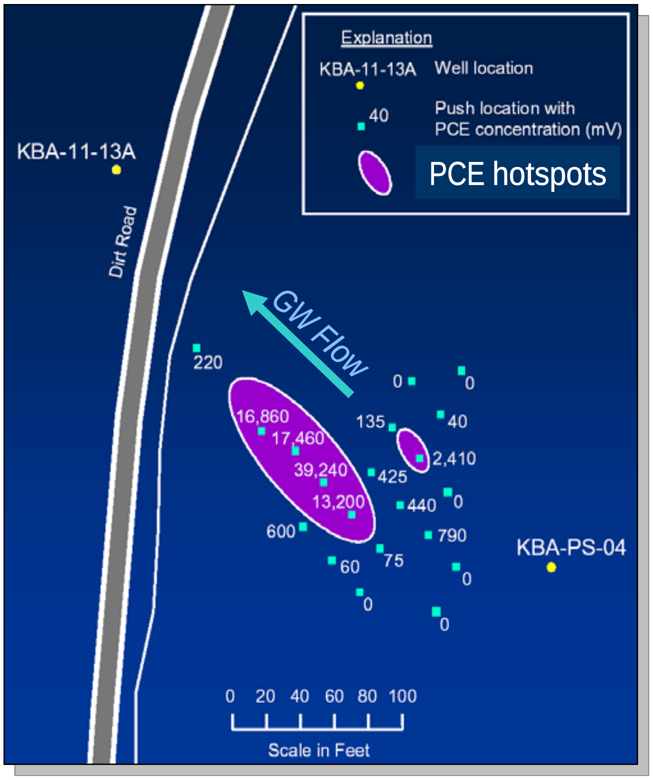

Figure A-1: Source Area at Kings Bay, GA (Casey, undated)

Selected Remedy:

In Situ Chemical Oxidation (ISCO) was chosen to limit downgradient migration. Four treatment campaigns were conducted between 1998 and 2001. A total of 48,000 gallons of 50% hydrogen peroxide and ferrous sulfate catalyst were injected in 23 wells to produce Fenton's reagent followed by 25,000 gallons of emulsified vegetable oil to provide a substrate for reductive chlorination. The injections were made into thin, permeable sand source zones, 30 to 42 feet below ground surface (bgs).

Results:

In the source zone between 1998 and 2004, vinyl chloride (VC), trichloroethylene (TCE) and cis-dichlorethylene (cis-DCE) all decreased after source treatment (Figure A-2). The treatment mobilized and/or increased advection of PCE, increasing its concentration significantly in the source area (Figure A-2). At a well USGS-9, 75 meters downgradient of the source area, cis-DCE and VC declined to ND (Figure A-3). At well USGS-11, also 75 meters downgradient of the treated source area, cis-DCE and VC concentrations changed with time (Figure A-3). Pump and treat appears to have driven cis-DCE and VC downgradient, but once pump and treat was stopped in 2001, ambient biodegradation was able to lower cis-DCE and VC levels. The considerable variability in the declining concentration reflects system complexity and the difficulty of choosing an effective DNAPL remedial technology for treating all contaminants. Site characteristics aiding source remediation included small, shallow, discrete sources and fairly simple, permeable media.

Conclusion:

In spite of a relatively small and homogenous site, the DNAPL remediation was more complex and expensive than anticipated, and some observations still cannot be adequately explained.

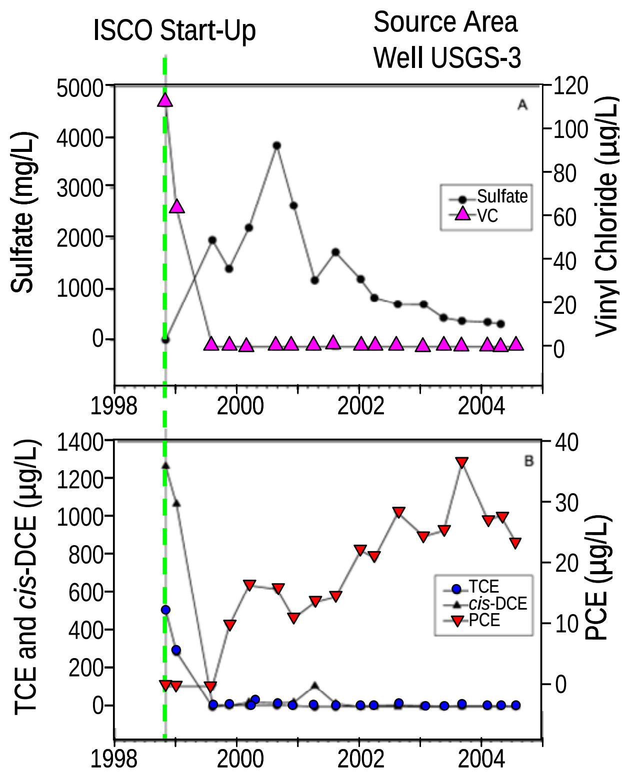

Figure A-2. Concentration Changes in the Treated Source Area Between 1998 and 2004 (Chapelle et al., 2005)

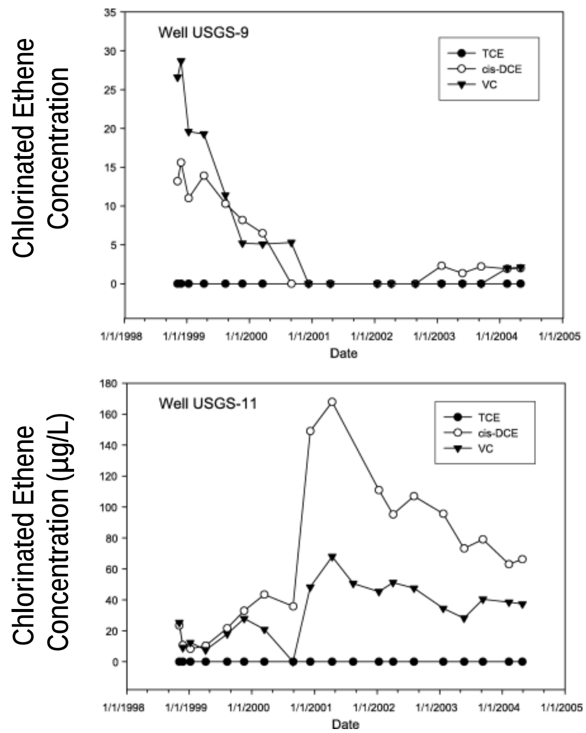

Figure A-3. Concentration Changes 75 m Downgradient of the Treated Source Area Between 1998 and 2004 (Chapelle et al., 2005)

Appendix B: Case Study 2—Example of a Large DNAPL Source Managed In Situ

Site Description:

In Salisbury, Maryland, a former Creosote Site left a large DNAPL contamination zone (Figure B-1). Groundwater flow at this site was directed toward the river (Figure B-2).

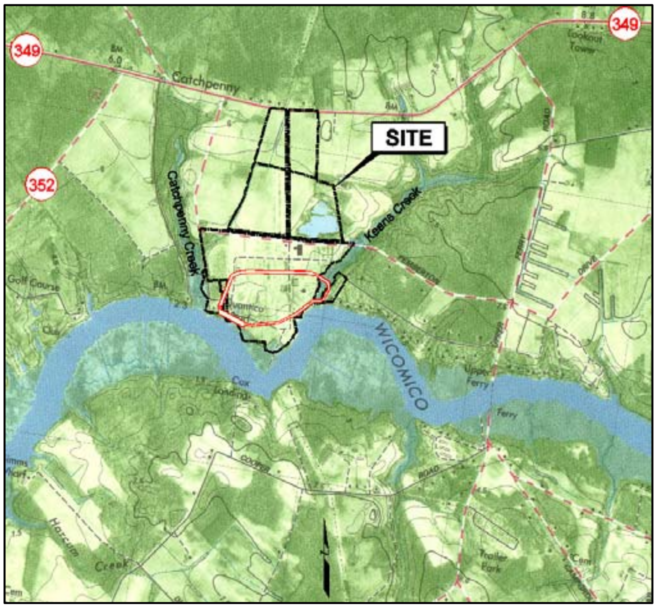

Figure B-1. Former Creosote Site, Salisbury, MD (RITS 2006: DNAPL Management Challenges)

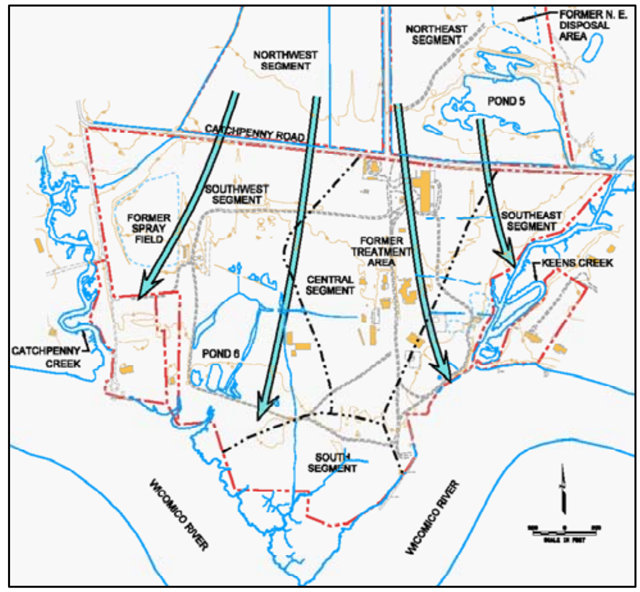

Figure B-2. Groundwater Flow at Creosote Site (RITS 2006: DNAPL Management Challenges)

Selected Remedy:

This site underwent multiple remedial activities costing between $10 and $11 million in capital expenses and approximately $200,000 annually for operation and maintenance. A barrier wall encircling 41.3 acres was installed to contain contamination, Keens Creek was rerouted to avoid passage through the contaminated site, new trees for phytoremediation and soil cover were applied to the site, and a shallow hydraulic gate was installed with air sparging just downgradient. In situ biological groundwater treatment and new wetlands constituted the on-site treatment. Product recovery systems were applied to the north and east portions of the site. See Figure B-3 for a layout of the remedial activities.

Results:

Risks were reduced primarily through containment. The State of Maryland awarded Beazer East, Inc., a Certificate of Merit for the containment and remedial activities.

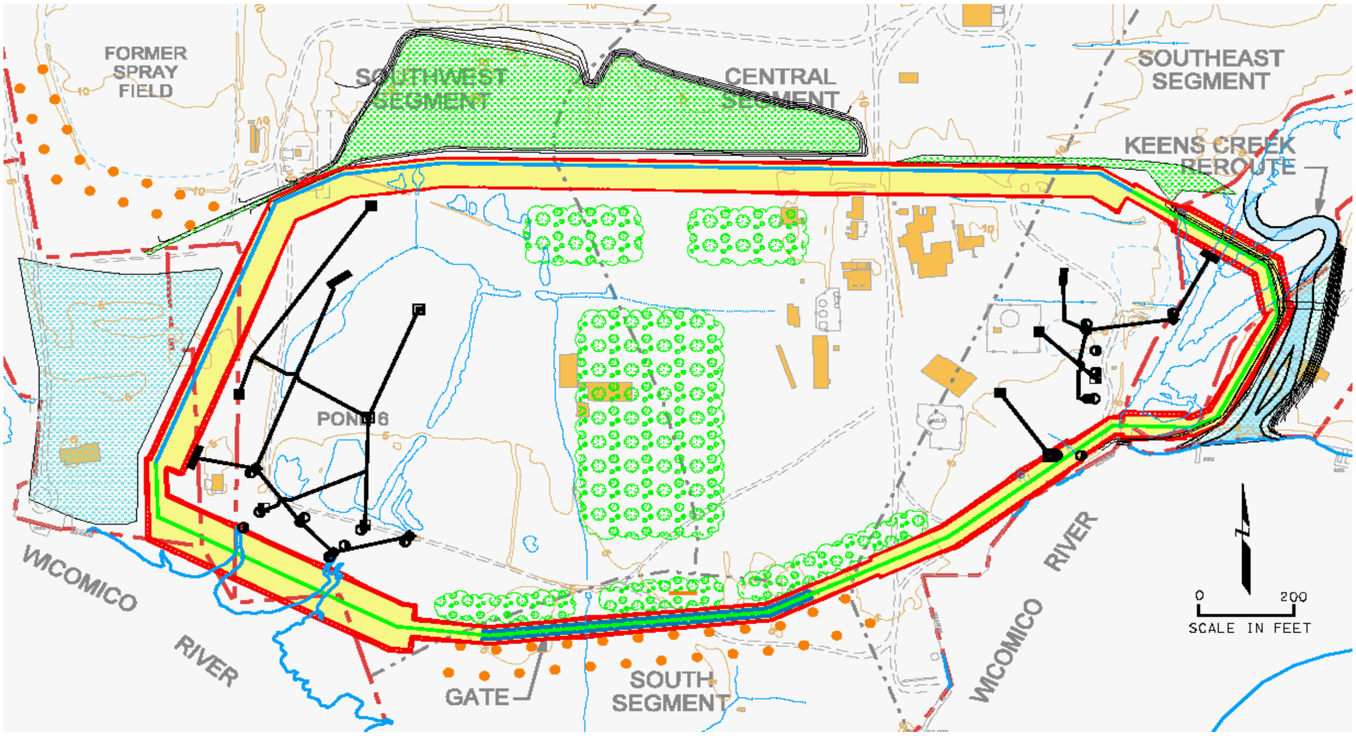

Figure B-3. Barrier Alignment, Hydraulic Gate, and Product Recovery Systems of Creosote Site (RITS 2006: DNAPL Management Challenges)

Conclusion:

The large complex site was managed well by understanding the limitation of technologies, the technical impracticability of complete source reduction, and using a combination of containment technologies to successfully reduce risks to health and the environment.