

Frequently Asked Questions Regarding Management of Chlorinated Solvents in Soils and Groundwater

July 2008

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Frequently Asked Questions

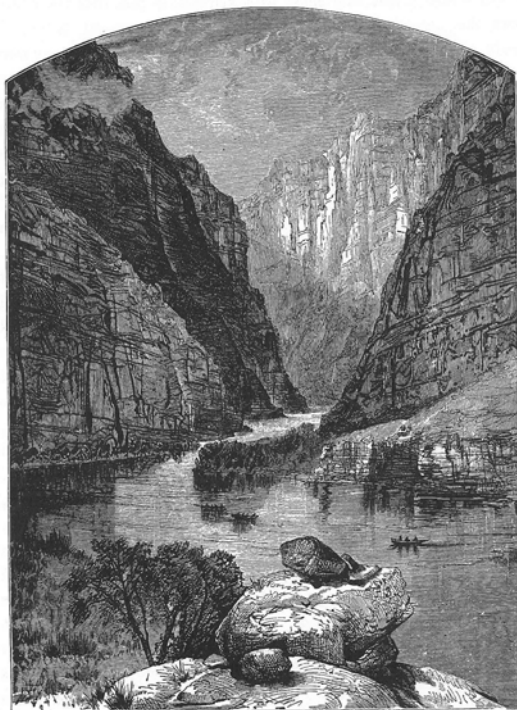
Regarding Management of Chlorinated Solvents in Soils and Groundwater

July 2008

Developed for the
Environmental Security
Technology Certification Program
(ESTCP)

by

Tom Sale, Charles Newell,
Hans Stroo, Robert Hinchee, and Paul Johnson



GATE OF LODORE.

More than 30 years ago, we set out on the journey of addressing releases of chlorinated solvents in soils and groundwater. Much like John Wesley Powell's exploration of the Colorado River and its tributaries (left), it has been a journey into the unknown. Fortunately, as was the case with Powell's endeavors, experience has been a keen instructor. Through the knowledge we have gained, we now stand well prepared to find pragmatic solutions for managing chlorinated solvents in subsurface environments.



This document is a product of the
Department of Defense Environmental Security
Technology Certification Program (ESTCP)

The following Frequently Asked Questions (FAQs) document provides a concise overview of current knowledge regarding management of subsurface chlorinated solvent releases. The envisioned audience is state regulators, federal regulators, consultants, Department of Defense (DoD) staff, and community members involved in selecting remedies for chlorinated solvent sites.

The document is intended to provide current knowledge in support of sound decisions. It is not intended to foster or discourage source zone treatment, but to help practitioners who are faced with difficult decisions, and to lay the groundwork for developing realistic expectations regarding the outcome of such treatments. Our hope is that the document contributes to better use of resources, more effective remediation and risk management, and more productive cooperation between the parties involved in site cleanups.

In the interest of brevity, the FAQs and the companion document ***Guide for Selecting Remedies for Subsurface Releases of Chlorinated Solvents*** assume that the reader has a general understanding of hydrogeology, the movement of chemicals in porous media, remediation technologies, and the overall remedy selection process.

The authors of this document wish to acknowledge the financial support of ESTCP for this project and the important contributions of researchers, scientists, and engineers who have built the knowledge base upon which this document stands. The authors also wish to acknowledge the invaluable contributions of reviewers from government, industry, academia, and the public at large who have supported this project.

Cover: Sand tank experiment conducted by Lee Ann Doner at Colorado State University evaluating contaminant storage and release in low permeability source zones. See FAQs 3 and 8.

TABLE OF CONTENTS

TECHNICAL CHALLENGES

1. What is the problem? 1
2. What are chlorinated solvents and why are they of concern?2
3. What happens when chlorinated solvents are released into the subsurface?3
4. What is a chlorinated solvent "source zone"?5
5. Why do we keep finding new challenges?6
6. Why is it common for source delineation efforts to miss a portion of a source?7
7. Why is it difficult to clean up aquifers by pumping out the contaminated groundwater?8

NEW THINKING

8. Why are contaminants in low permeability zones important?9
9. Why are contaminants that are above the water table important? 11
10. What have we learned in the last half century 12
11. What types of goals can we set for chlorinated solvent releases 13

SOURCE TREATMENT

12. Which in situ source treatment technologies are receiving the widest use? 14
13. What can we expect from common source treatment technologies? 15
14. How much does it cost to treat source zones? 17
15. How will reduced loading from sources affect plumes? 18
16. What are the effects of source treatment on cleanup time frames? 20

ALTERNATIVES TO SOURCE TREATMENT

17. Which containment measures are receiving the widest use?21
18. What can we expect from containment measures?22
19. How much does containment cost?23
20. How does one compare treatment versus containment? 24

MAKING DECISIONS

21. How do site characteristics affect cleanup decisions?25
22. Taking stock: In retrospect, why have we not been more successful?27
23. How can we set cleanup objectives that are attainable and beneficial? 28

WHERE DO WE GO FROM HERE?

24. How can we be more successful at site cleanup? 30
25. Where can I find more information? 31

REFERENCES.....32

AUTHORS.....34

1. What is the problem?

From automobiles and airplanes to computers and systems for national defense, chlorinated solvents have been central to modern life. Unfortunately, from the 1940s into the 1980s, storage and disposal practices for chlorinated solvents frequently resulted in releases into soil and groundwater. In hindsight, these flawed practices reflected a misunderstanding of the environmental impacts of what was being done. Regrettably, this theme is common to many environmental issues.

Since the late 1970s, we have been engaged in managing the legacy of our past practices. Through investing many tens of billions of dollars, we have dramatically reduced the frequency of chlorinated solvent releases, characterized the impacts and risks at tens of thousands of sites, and developed several remediation technologies that show promise in removing contaminants from the subsurface.

However, technical challenges make it very difficult or impossible to completely clean up these sites, and the costs for chlorinated solvent remediation can be very high. Further, there are significant uncertainties involved in predicting the benefits of chlorinated solvent site remediation. As a result, site stakeholders face difficult decisions regarding selection and design of appropriate remediation strategies.

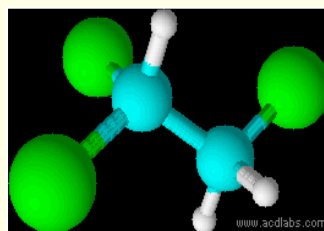
We have discovered that characterizing and managing chlorinated solvent-impacted sites is more difficult than we had first thought. At the same time, through research programs such as ESTCP and the Strategic Environmental Research and Development Program (SERDP) and experience gained at field sites, remediation science and engineering has improved dramatically. Given what we now know, we can be more successful in the future than we have been in the past.



1950s chlorinated solvent disposal area

2. What are chlorinated solvents and why are they of concern?

Chlorinated solvents are typically composed of one or two carbon atoms and between one and six chlorine atoms. They were first produced in Germany in the 1800s, and widespread use in the U.S. began after World War II. In the period of 1940-1980, the U.S. produced about 2 billion pounds of chlorinated solvents each year (Pankow and Cherry, 1996). Common chlorinated solvents such as trichloroethene (TCE), perchloroethene (PCE), trichloroethane (TCA), and carbon tetrachloride (CT) have been used for a variety of purposes, including dry cleaning, degreasing, cleaning, pesticide manufacturing, and chemical intermediates.



Trichloroethane (TCA) - C₂H₃Cl₃

From an industrial perspective, chlorinated solvents have many desirable attributes. Unfortunately, in subsurface environments, these same attributes can create significant challenges (see table below).

Attributes, industrial values, and environmental challenges of chlorinated solvents

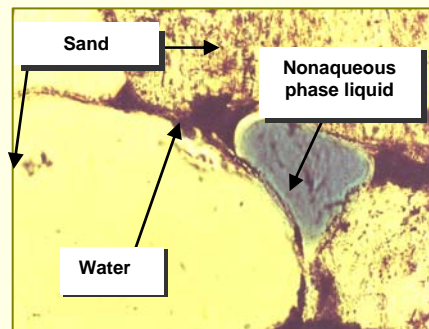
| Attribute | Industrial Values | Environmental Challenges |
|--|---|---|
| Volatile | Good for cleaning | Readily form vapor plumes in soils |
| Chemically stable under typical aerobic conditions | Easy to store | Often slow to degrade in aerobic soils and groundwater systems |
| Many are nonflammable | Typically not a fire or explosion hazard | Stable under natural aerobic conditions |
| Slightly soluble in water | Remains in a separate liquid phase when mixed with water (immiscible) | Small releases can contaminate large amounts of water and persist as sources for long periods of time |
| Densities much greater than water | Easy to separate from water | Can sink through water-saturated media (e.g., aquifers and aquitards), contaminating water deep underground |
| Low viscosity | Easy to apply to surfaces | Can move quickly through subsurface environments |

Perhaps the most fundamental problem is that most of the commonly used chlorinated solvents are classified as actual or potential cancer-causing compounds and are therefore subject to stringent drinking water standards. For example, many chlorinated solvents are considered to present health risks if ingested in drinking water at concentrations greater than 5 micrograms per liter (5 parts per billion). When this drinking water standard (called the maximum contaminant level, or [MCL]) is compared to concentrations of hundreds or thousands of parts per billion that are commonly observed in groundwater at chlorinated solvent sites, it becomes apparent that a small solvent release can cause a large environmental problem. For example, one liter of TCE can theoretically contaminate 50 million gallons of water with TCE at a concentration above the drinking water standard. At some sites, vapors from groundwater plumes can also cause unacceptable risks.

Today, the number, size, and persistence of chlorinated solvent sites have culminated in a significant environmental problem. There are an estimated 15,000 to 25,000 chlorinated solvent sites in the United States, with groundwater plumes typically ranging from 500 to 5,000 feet in length. The plumes we see today were largely caused by releases that occurred in the 1960s, 1970s, and 1980s, illustrating the persistent long-term aspects of the chlorinated solvent problem.

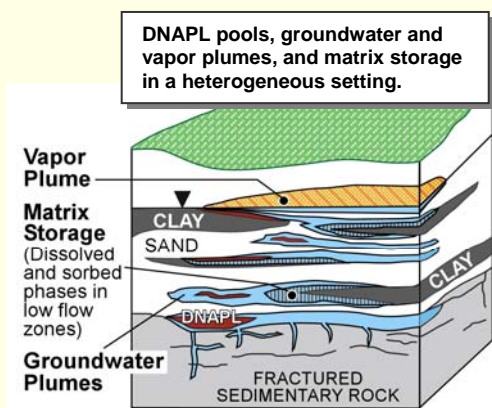
3. What happens when chlorinated solvents are released into the subsurface?

Typically, chlorinated solvents were released into soil or groundwater as a liquid that was immiscible with and denser than water. Liquids with these properties are referred to as dense non-aqueous phase liquids (DNAPLs). In the subsurface, DNAPLs are driven downward through soil pores by gravity. Initially, DNAPL displaces air and/or water from the pore space. Then, as the DNAPL drains out, it often leaves a trail of residual blobs or ganglia of DNAPL held in place by capillary forces. A photo of water and a nonaqueous phase liquid sharing the pore space between sand grains is presented in the adjacent photograph.



Nonaqueous phase liquid and water sharing pore space in sand (Wilson et al., 1990)

DNAPL can also form continuous bodies referred to as pools. As shown in the figure below, pools frequently occur on top of low permeability layers. Permeability describes the capacity of a porous media to transmit fluids. Where DNAPL is present, compounds in the DNAPL will dissolve into water, sorb to solids, and partition into soil gas. This leads to the observation that managing chlorinated solvents is not just about managing DNAPL, it is also about managing chlorinated solvents dissolved in water, sorbed to solids, and volatilized in soil gas.

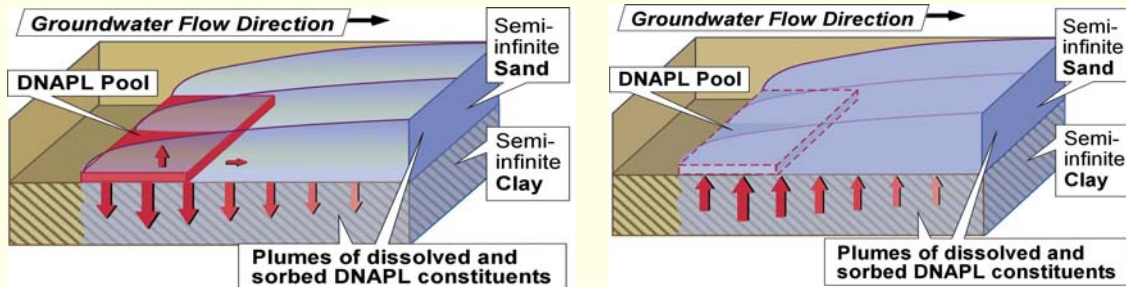


Further insight into the evolution of a chlorinated solvent release is gained by recognizing that subsurface environments almost always contain complex distributions of different geologic media that have widely varying capacities to transmit fluids (permeability). Geologic complexity and the associated spatial variations in permeability are widely referred to as heterogeneity. The adjacent graphic portrays a heterogeneous setting, with sand and clay layers interbedded above fractured sedimentary rock in which the rock blocks, or matrix, have significant porosity.

There are two main consequences of heterogeneity. First, DNAPLs preferentially move through sediment with the greatest permeability. DNAPL is largely precluded from entering low permeability by capillary forces. An important exception occurs where secondary features such as fractures, root casts, or animal borings are present in low permeability layers. In the end, subsurface DNAPL occurrence is often conceptualized as sparsely distributed fingers of DNAPL ganglia and pools. Intervals where DNAPL is present are surrounded by intervals that are largely free of DNAPL. The sparse distribution of DNAPL partially explains why it is difficult to find DNAPL. A comprehensive review of DNAPL transport and occurrence is presented in Pankow and Cherry (1996).

The second consequence of heterogeneity is that subsurface environments are composed of intervals where water is moving (transmissive zones) and intervals where water is largely immobile (low permeability zones). Over time, constituents in DNAPL dissolve in water and/or volatilize into soil gas. This process leads to plume formation in transmissive zones where there is flow. At the same time, high concentrations of dissolved contaminants in transmissive zones drive contaminants into low permeability zones via diffusion. Within low permeability zones, contaminants are stored as a dissolved phase in water and as a sorbed phase on or in solids. The topic of contaminants in low permeability zones receives further attention in FAQ 8, *Why are contaminants in low permeability zones important?*

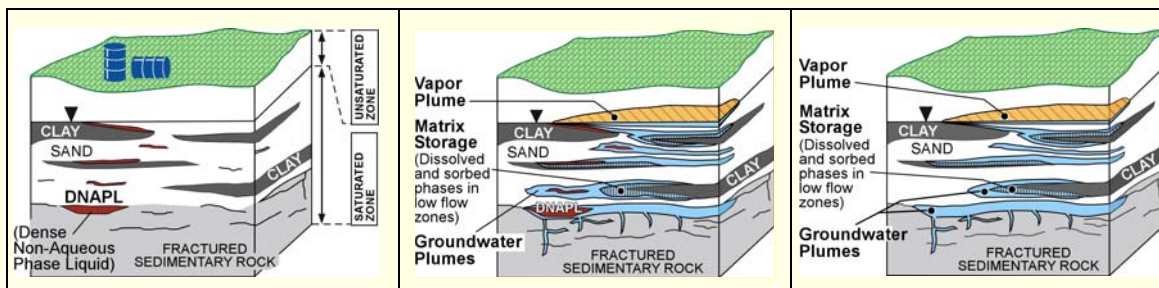
The process of contaminants moving into low permeability layers via diffusion is referred to as *matrix diffusion*. The significance of contaminants in low permeability layers is that they can sustain dissolved plumes in transmissive zones long after the DNAPL source is gone (e.g., Chapman and Parker, 2005; AFCEE, 2007). The process by which contaminants are stored and released from low permeability zones is illustrated in the figures below.



Diffusion of contaminants into a low permeability zone beneath a DNAPL pool and the downgradient plume. (Arrows show movement of dissolved solvents.)

Diffusion of contaminants out of a low permeability zone after complete DNAPL depletion (Arrows show movement of dissolved solvents.)

With time, subsurface chlorinated solvent releases age. Early in their lives, they are dominated by DNAPL, but slowly DNAPLs dissolve, plumes develop, and contaminants accumulate in permeable zones. Eventually, little to no DNAPL remains, and plumes are sustained by the release of contaminants from low permeability zones via diffusion (Chapman and Parker, 2005). Although recoverable DNAPL can still be found within some source zones, it is notoriously difficult to find DNAPLs at the heads of many persistent plumes. At some sites (see late stage below), it simply may not be there any longer, even though the source zone (see FAQ 4) is still active. Key factors controlling the rate at which chlorinated solvent releases age include the amount of DNAPL released, the solubility of the constituent in the DNAPL, the rate of groundwater flow, and the architecture of transmissive and low permeability zones.



EARLY STAGE

MIDDLE STAGE

LATE STAGE

Aging of a chlorinated solvent release

Note that DNAPLs are not present at all sites impacted by chlorinated solvents. For example, chlorinated solvents dissolved in process water were discharged to soil and groundwater at some sites, and in other instances, chlorinated solvents were mixed with light nonaqueous phase liquids (LNAPLs) (i.e., fuels or oils) prior to discharge. While there are important differences between these release mechanisms, many of the ideas presented herein still apply.

4. What is a chlorinated solvent “source zone”?

A 2005 National Research Council report (NRC, 2005) defines a chlorinated solvent source zone as a subsurface reservoir that a) initially contains DNAPL and b) sustains plumes (primarily dissolved groundwater plumes). (Note: this concept can also apply to vapor plumes. See FAQs 3, 5, and 10.) Furthermore, NRC (2005) states that the DNAPL-containing region is initially the primary reservoir but that the source zone also includes high concentration dissolved- and sorbed-phase halos around the DNAPL region. NRC (2005) also recognizes that some chlorinated source zones are depleted of DNAPL and that the high-concentration halo can be a reservoir that sustains plumes.

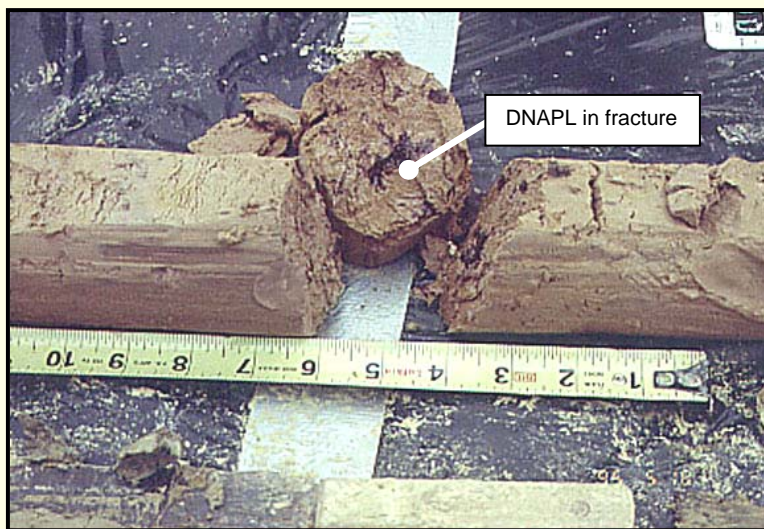
At many sites, the problematic source zone is below the water table in the “saturated zone”. This document focuses primarily on saturated zone issues. At some sites, sources are present above the water table in the “unsaturated zone”. This occurs most frequently at sites with large depths to groundwater. Attributes of chlorinated solvents in the unsaturated zone are addressed in FAQs 3, 5, 9, 10, and 12.

Early in the life of a DNAPL release, the DNAPL-impacted source zone will contain the majority of the chlorinated solvent mass. Later, after DNAPL has been depleted via dissolution, volatilization, and/or remedial measures, the remaining mass may reside beyond the original DNAPL in transmissive and low permeability zones (as discussed in FAQs 3 and 8). Given only limited DNAPL, it can be difficult to determine where the source zone ends and the plume begins. In particular, this is true for the “late stage” chlorinated solvent release introduced in FAQ 3.

In some rare cases, chlorinated solvents were released as a high concentration phase dissolved in water. In these cases, dissolved and sorbed phase solvents that accumulate in low permeability zones may behave as a source even though no DNAPL was released. Again, delineation of where the source ends and the plume begins can be difficult in this situation.

Another variant is the release of chlorinated solvents dissolved in petroleum liquids. In this case, biological degradation of soluble petroleum-based compounds can drive reductive dechlorination of aqueous phase chlorinated solvents. This can potentially limit the formation of plumes in transmissive zones and the accumulation of contaminants in low permeability zones.

A photo of a soil core collected from below the water table in a DNAPL source zone is shown below. DNAPL occurrence in the source zone soil is sparse. However, the silty clay soil matrix adjacent to the DNAPL provides an extensive body for contaminant storage in dissolved and sorbed phases.

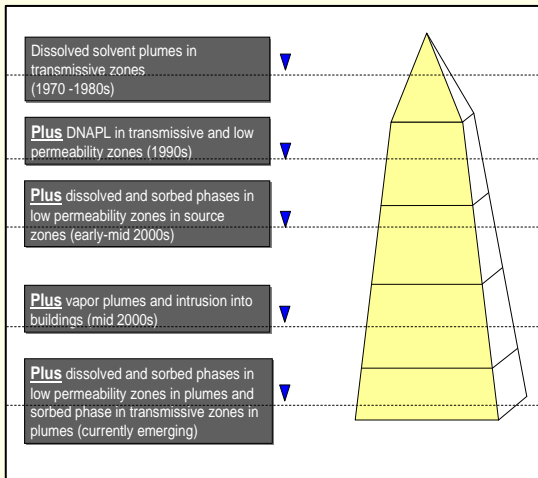


Core from a DNAPL source zone collected below the water table.
DNAPL is present in a fracture within a silty clay soil.

5. Why do we keep finding new challenges?

As shown in the adjacent figure, our emerging understanding of the chlorinated solvent problem resembles slowly draining a lake containing a submerged monument.

- Prior to the 1970s, the problem of chlorinated solvents in groundwater was fully submerged.
- By the 1970s and 1980s, the issue of dissolved phase contamination in the transmissive portions of aquifers had emerged.
- Limited successes in addressing dissolved phase chlorinated solvents in the 1970s and 1980s via pumping (see FAQ 7) led to the emergence of DNAPL as a critical focus in the 1990s.
- By the early to mid 2000s, persistent source zones with little or no DNAPL led to recognition of dissolved and sorbed phase contaminants in low permeability zones as yet another target for chlorinated solvent remediation efforts.
- Furthermore, by the mid 2000s, contaminants present in vapor plumes and their impacts on indoor air became a driver for remedial action.
- Most recently, we are learning that large amounts of chlorinated solvents can be stored in plumes as a slowly desorbing phase in transmissive zones, and/or as sorbed and dissolved phases in low permeability zones (e.g., Chapman and Parker, 2005). Additionally, new contaminants of concern associated with chlorinated solvents are emerging, such as 1,4 dioxane and 1,2,3-trichloropropane.



Emerging focus of chlorinated solvent remediation efforts (note the importance of each level depends on the site condition including the stage of the release (see FAQ 3))

Building on the above discussion and the information from FAQs 3 and 4, a 14-compartment model for chlorinated solvent releases is advanced in the figure below. The model identifies four zones with low permeability and transmissive zones in sources and plumes. In source zones, chlorinated solvents can be present as a vapor, DNAPL, aqueous, or sorbed phase. In plumes they can be present as a vapor, aqueous, or sorbed phases.

| Phase / Zone | Source Zone | | Plume | |
|--------------|------------------|--------------|----------------|------------------|
| | Low Permeability | Transmissive | Transmissive | Low Permeability |
| Vapor | | | | |
| DNAPL | | | Not Applicable | |
| Aqueous | | | | |
| Sorbed | | | | |

Fourteen-compartment model showing compartments potentially containing chlorinated solvents (per NRC, 2005). DNAPL is not present in plumes. Arrows illustrate contaminant transfer links between zones and phases.

The 14-compartment model has many uses, including helping us to understand why we have been finding new challenges. First, our site characterization approaches have often illuminated only a portion of the problem. As an example, water quality data from conventional monitoring wells help us resolve the aqueous phase chlorinated solvents in transmissive zones. Unfortunately, they often provide little insight regarding any phase in low permeability zones or vapor, DNAPL, or sorbed phase in transmissive zones. Secondly, most of our technologies only address select compartments, and in doing so they can reveal what we have missed. As an example, pump-and-treat depletes aqueous phase contaminants from transmissive zones. However, sustained aqueous concentrations illuminate the importance of the presence of contaminants in any phase in low permeability zones and/or vapor, DNAPL, and sorbed phases in transmissive zones.

6. Why is it common for source delineation efforts to miss a portion of a source?

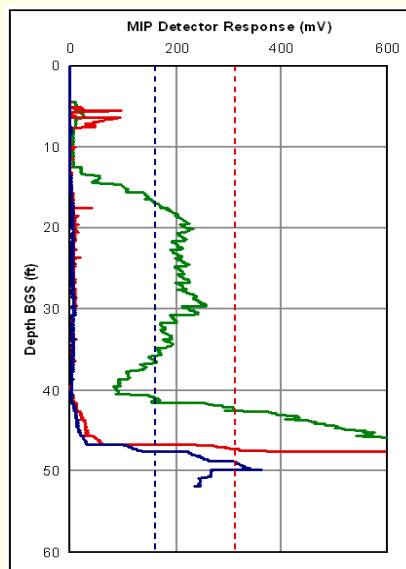
All too often, post-remediation data suggests that initial site characterization and remediation efforts missed a portion of a source zone. This has been a common experience with excavation remedies. Initial soil coring-based investigations lead to definition of a targeted volume, but inspection of material during the excavation typically results in realization of a larger volume requiring treatment. Another example is the installation of bentonite slurry walls around source zones. Detailed delineation results in an assumed “clean line” along the alignment of the barrier. During construction, however, contamination can be found in this supposed clean area.

In retrospect, this raises the question: Why aren't we better at delineating source zones? Answers include:

- Due to pragmatic constraints, decisions are often made using a limited dataset that has insufficient resolution.
- Chlorinated solvent releases typically involve heterogeneous distributions of DNAPL and other contaminant phases that are difficult to quantify (see FAQ 3).
- Common reliance on groundwater data collected from wells with long screen intervals in transmissive zones provides limited insight into the distribution of DNAPL, sorbed phase, vapor phase, or mass stored in low permeability zones.
- At older release sites, DNAPL may have dissolved away, and we often fail to look in low permeability zones that can be the primary source of persistent releases to plumes.
- It is difficult to resolve where the source ends and the plume begins at the downgradient edge of the source zone. This reflects the fact that large amounts of contaminant can be stored in downgradient low permeability zones immediately beyond the space in which DNAPL was originally present.
- Site characterization is often de-emphasized in a rush to install a source zone remediation system. More often than not, the source zone is larger than initially thought, but this is only realized after the initial remediation attempts, requiring iterative characterization and remediation efforts.

New site characterization technologies, such as instrumented direct-push devices (i.e., rapid optical screening techniques [ROST], membrane interface probe [MIP] [see log to the right], and dye-coated tapes are helping to improve site characterization programs. However, all too often, the best that can be done with source delineation is to rely on an iterative approach (see FAQ 24). Typically this involves using the available data to make a conservative best estimate of the extent of the source, develop contingency plans should a significant portion of the source be missed, and recognize that, based on experience to date, a portion of the source is likely to remain. Helpful summaries of source delineation methods can be found in Cohen and Mercer (1993); Rossabi et al., (2000); Pankow and Cherry (1996); and ITRC (2003b).

Right - Example of a MIP log showing the relative distribution of a chlorinated solvent. Red line - photoionization detector (PID); Blue line - dry electrolytic conductivity detector (CD); and green line - flame ionization detector (FID)



7. Why is it difficult to clean up aquifers by pumping out the contaminated groundwater?

The earliest efforts to clean up chlorinated solvent releases involved simply removing contaminated groundwater from transmissive zones. The premise was that contaminated water could be drawn out of aquifers in the same way that it might be drained from a tank. Unfortunately, experience has taught us that contaminants stored in other compartments (gas in soil, sorbed to solids, dissolved in groundwater in low permeability zones, and DNAPL) act as reservoirs, sustaining contaminants in groundwater.

One of the earliest commentaries on pumping as a remedial scheme is provided by Matis (1971):

"Over a period of time pumping may remove some of the contamination. Although we have advised use of this technique for cases of minor contamination, it has not definitely proven successful....With regard to clean up activities, it may be (and often is) impossible to remove the contaminant from ground water."

One of the most comprehensive efforts to evaluate groundwater pump-and-treat systems was the U.S. Environmental Protection Agency's (USEPA's) *Evaluation of Ground-Water Extraction Remedies*, published in 1989. The USEPA studied 18 pump-and-treat systems that had been operating for up to 15 years and drew the following conclusions:

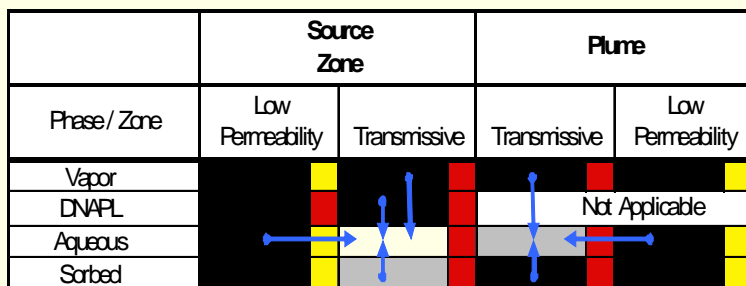
- The systems were generally effective at containing the plumes and removing mass.
- Groundwater concentrations decrease rapidly at startup, then level off at a "greatly reduced rate" where progress toward aquifer restoration was usually proceeding "slower than expected".
- Factors constraining groundwater restoration included system design, sorption, effect of low-permeability zones, and presence of NAPLs and leaching from the vadose zone.

The National Research Council's 1994 report on groundwater cleanup alternatives concluded:

"Remediation by pump and treat processes is a slow process. Simple calculations for a variety of typical situations show that predicted clean-up times range from a few years to tens, hundreds, or even thousands of years."

Given the rate of contaminant mass removed by typical groundwater extraction wells, and the likely original mass in place, the time required to significantly deplete released solvents by groundwater pumping has proven to be long (i.e., decades). In defense of groundwater extraction, it is a proven, robust technology for controlling the migration of groundwater plumes (see FAQ 18) and is often a viable, near-term solution. Unfortunately, pumping groundwater for containment is often perceived to be economically burdensome as years stretch to decades and beyond.

A comprehensive answer to the question of why is it difficult to clean up aquifers by pumping can be developed using the 14-compartment model introduced in FAQ 5 and applied in the figure below. Depleting aqueous phase contaminants from transmissive zones simply results in further releases of contaminants from contaminants in low permeability zones and/or vapor, DNAPL, and sorbed phases in transmissive zones. Dealing with a portion of the problem only leads to recognition of what was missed.



An illustration of the potential effectiveness of pump-and-treat at a hypothetical site using the 14-compartment model. Red and yellow indicate compartment with high and moderate levels of chlorinated solvents, respectively. White, gray, and black indicate high to low levels of contaminant depletion anticipated from application of pump-and-treat in the source. Arrows indicate induced release of contaminants from compartments that are not directly affected by pump and treat.

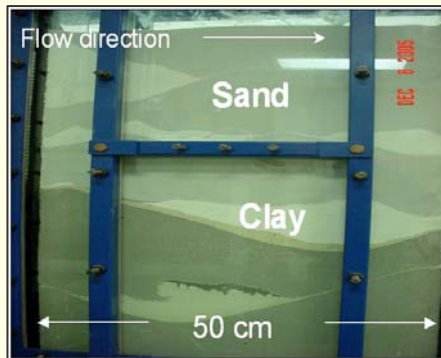
8. Why are contaminants in low permeability zones important?

Abrupt contacts between transmissive zones (e.g., sand) and comparatively stagnant low permeability zones (e.g., clay) are common in geologic media. Interbedded layers of geologic media are illustrated in the rock sample to the right and in the sand tank below.

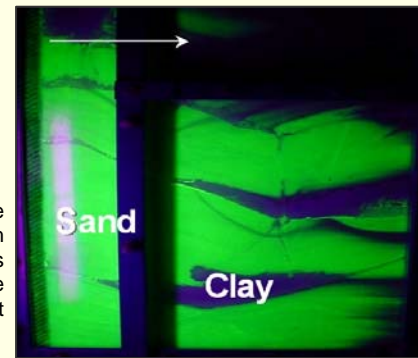


Interbedded transmissive (sandstone) and low permeability zones (shale).

As discussed in FAQ 3, DNAPL or dissolved phase contamination initially moves preferentially through the pathway with the greatest permeability. This is illustrated in the sand tank pictured below, where water dyed with green fluorescein is being pumped through a tank containing layers of sand and clay. Initially, little or no contamination is present in the lower permeability clay layers.

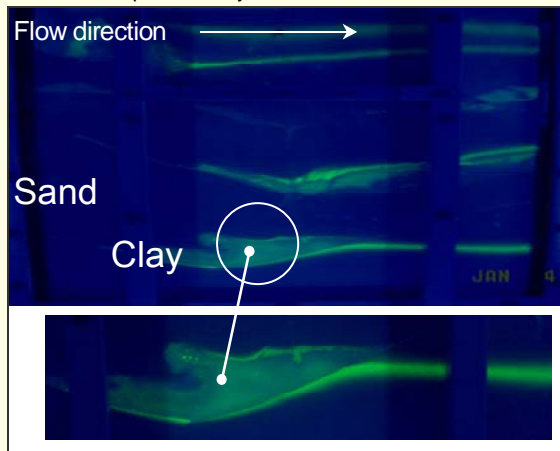


Laboratory sand tanks with sand and clay layers



Fluorescein dye moving through sand layers early in the experiment

Flushing with clean water leads to the release of contaminant stored in low permeability zones



With time, dissolved phase contaminants migrate into the low permeability clay layers via diffusion and/or slow advection. Contaminants in the clay layers are stored in dissolved and sorbed phases. In some cases, DNAPL can also be present in low permeability layers.

Most natural processes and remediation technologies preferentially deplete chlorinated solvents in transmissive zones. When this occurs, contaminants are released from the low permeability zones back into the transmissive zones via diffusion and slow advection. The release process is illustrated by the trails of water with green fluorescein dye emanating from the clay layers in the image on the left.

The degree to which contaminants stored in low permeability zones (matrix storage) can sustain dissolved plumes depends on site conditions. General conditions driving matrix storage effects include:

- Geologic settings with transmissive zones that are a small fraction of the aquifer's total volume
- Contaminants that are present at high concentrations
- Contaminants that are stable in their physical setting (e.g., TCE in an aerobic aquifer)
- Systems with relatively slow groundwater flow rates
- Sediments with high fractions of organic carbon
- Sites where large amounts of contaminant were released
- Older sites where there has been a large amount of time for contaminants to move into low permeability zones.

Sites where the inverse of the above is true will have less significant matrix storage effects. One of the most important conditions that can limit matrix storage effects is having active in situ attenuation of contaminants via biological or chemical processes. In this case, contaminant accumulation and subsequent release from low permeability zones may be limited by ongoing degradation of contaminants.

Primary implications of active matrix storage include the following:

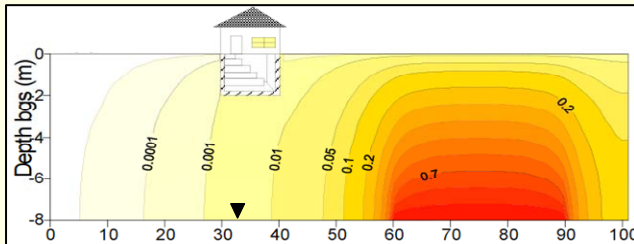
- Release of stored contaminants can sustain contaminant discharge from source zones for long time periods. This can explain the persistence of low-level dissolved plumes where little or no DNAPL can be found.
- Given near-perfect depletion and/or containment of sources, downgradient plumes may still persist for extended periods (i.e., decades) as a result of downgradient matrix storage effects in the plume.
- Source zone treatments that solely address transmissive zones may miss substantial contaminant mass in low flow zones and be subject to rebound.

An example of how low permeability zones affect plume cleanup is presented in FAQ 15.

Advancing the issue of contaminants in low permeability zones is not intended to discourage efforts to clean up sites. Its value is to support a comprehensive understanding of the potential challenges associated with subsurface releases of chlorinated solvents. Furthermore, it adds emphasis to the fact that cleaning up chlorinated solvent releases may involve more than simply depleting DNAPLs.

9. Why are contaminants that are above the water table important?

At select sites chlorinated solvents may be present above the water table as vapor, DNAPL, aqueous, and/or sorbed phases (FAQs 3 and 5). Chlorinated solvents above the water table can impact underlying groundwater via leaching (downward flow of water through the unsaturated zone) and/or diffusion driven transport through soil gas. Alternatively, vapor phase chlorinated solvents can move via advection and/or diffusion into buildings and/or confined spaces where exposure via inhalation can be an issue. In the case of indoor air, the source can be chlorinated solvents stored in the unsaturated zone and/or, as shown below, chlorinated solvents originating from groundwater in the vicinity of the water table.



An example of a volatile compound in groundwater moving from the water table to a building under negative pressure in homogeneous setting. Isoconcentration lines depict dilution of the volatile compound as a function of position. Adapted from Abreu and Johnson (2005)

An interesting aspect of vapor phase transport is that diffusion coefficients are approximately four orders of magnitude greater in air than they are in water. In media with low water content, diffusion can drive rapid transport over large distances as compared to groundwater systems. One ramification of this is that the persistence of chlorinated solvents in media with low water content is often limited due to rapid natural depletion via diffusion. On the other hand, as water content increases, transport of vapor phase solvents becomes constrained by reduced air-filled pore space, greater tortuosity of pathways, and accumulation of aqueous phase contaminants in pore water. At the extreme, local layers of fine-grained media in the unsaturated zone are often fully saturated with water. These layers form effective barriers to vapor phase transport. Furthermore, they can accumulate aqueous and sorbed phase contaminants over time and act as persistent sources (much like low permeability zones below the water table).

The development of analytical models that use partitioning and subsurface vapor transport to estimate indoor air concentrations (Johnson and Ettinger, 1991; U.S. EPA, 2007) has been a crucial step in increasing our understanding of vapor intrusion. Unfortunately, determining if subsurface releases of chlorinated solvents are impacting indoor air can be difficult. Confounding factors include:

- High background concentrations of chlorinated solvents in buildings can make it hard to distinguish groundwater versus indoor sources
- High temporal and spatial variability in subsurface vapor and indoor air data
- Expense in collecting vapor data.








ESTCP has funded projects to increase our understanding of this critical migration pathway by developing new sensors (ER-0702) and performing studies at field sites with extremely high data density (ER-0423 and ER-0707). Some preliminary results show that:

- Air-flow across building foundations is bi-directional resulting in transport of volatile organic compounds (VOCs) from indoor sources to the subsurface.
- Tracer gases, such as naturally-occurring radon, help distinguish between subsurface and indoor sources of chlorinated solvents in buildings.
- Mass flux measurements in groundwater can be helpful to put an upper limit on indoor air exposure in buildings.

10. What have we learned in the last half century?

Over the last 50 years, our understanding of the behavior of chlorinated solvents in soils and groundwater has matured. Several broadly accepted tenets have been displaced by new knowledge, and with this, we are now in a far better position to make sound decisions than we were in the past. The following table provides a review of key paradigm shifts that have come about in the past half century.

Chlorinated solvent paradigm shifts of the last half century

| Old School Paradigm (Period of prevalence) | | New School Paradigm (Time of broad acceptance) |
|---|---|--|
| Given the volatility of chlorinated solvents, land disposal is an appropriate practice. <i>(1940s through 1970s)</i> |  | Releases of chlorinated solvents to subsurface environments can create big problems. Few things are more important than limiting future releases. <i>(Beginning in the 1980s)</i> |
| Aquifers may be restored by pumping out the contaminated water (pump and treat). <i>(1970s through 1980s)</i> |  | Solvents sorbed to solids, present as DNAPL, and stored in low permeability zones can sustain groundwater concentrations in transmissive zones for long periods. <i>(1990s through 2000s)</i> |
| Chlorinated solvents are recalcitrant. <i>(1970s through 1990s)</i> |  | Chlorinated solvents will degrade under a range of natural and engineered conditions. <i>(Beginning late 1990s)</i> |
| Emerging technologies will frequently achieve MCLs in source zones. <i>(early to mid 1990s)</i> |  | Our experience to date indicates attaining MCLs throughout source zones has been very rare. Nevertheless, significant mass depletion has been achieved and technologies continue to improve. <i>(Beginning mid 1990s)</i> |
| Primary risks and site care costs can be addressed by removal and/or depletion of source zones. <i>(1970s through early 2000s)</i> |  | Contaminants often remain after source zone treatment in source zones and plumes. What remains can sustain exceedances of MCLs and necessitate site care for long periods of time. <i>(Mid 2000s)</i> |
| Source zone remediation is a necessary component of corrective action. <i>(1970s through early 2000s)</i> |  | Source zone remediation should be considered but is not always a necessary component of corrective action. Long-term management, containment, and monitored natural attenuation (MNA) may be adequate and more cost-effective strategies at some sites. <i>(2000s)</i> |
| Groundwater represents the primary pathway and media of concern. <i>(1970s through late 1990s)</i> |  | Vapor intrusion is recognized as a pathway of concern of the same order as groundwater. <i>(2000s)</i> |

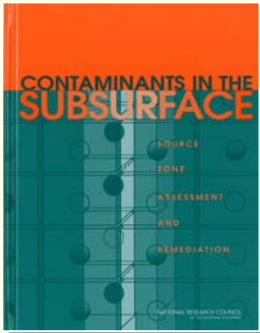
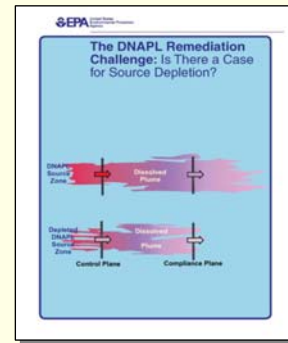
Perhaps the best news about being better informed is that we can now avoid the mistakes of the past. By discarding the paradigms from the left side of the table and moving on to those on the right, we have enormously improved our chances of successfully managing chlorinated solvents.

11. What types of goals can we set for chlorinated solvent releases?

Ideally, remediation would achieve complete and quick restoration of the source zone and related plumes. Unfortunately, this ideal has proven elusive at most sites impacted by chlorinated solvents. Most experts agree that restoration to risk-based criteria will generally require long periods of time and perhaps the use of several technologies at different times and locations. With this there can be a perception of an unending need to do more regardless of what is done, and the gridlock of pondering why one should ever get started with remediation if it will never be done. As a result, rigorous cleanup goals can distract us from pursuing beneficial and attainable near-term results. Building on these themes, Kavanaugh et al. (2003), an expert panel study funded by the USEPA and NRC (2005), a National Research Council Report funded by the U.S. Army, discuss potential alternative goals for chlorinated solvent releases.

The DNAPL Remediation Challenge – Is there a Case for Source Depletion (Kavanaugh et al., 2003) offers:

- Reduce potential for DNAPL migration as a separate phase
- Reduce source longevity and reduce long-term management requirements
- Reduce mass flux—the rate at which contamination is feeding a groundwater plume
- Enhance the effectiveness of complementary technologies
- Stabilize the extent of plumes
- Reduced life-cycle costs
- Achieving intangible benefits such as reducing the burden to future generations



Contaminants in the Subsurface – Source Zone Assessment and Remediation (NRC, 2005) offers:

- Deplete the source zones
- Reduce concentrations in source zones
- Reduce contaminant flux from source zones
- Reduce DNAPL migration potential
- Reduce plume size
- Reduce contaminant toxicity
- Eliminate barriers to subsequent remedial actions
- Reduce life-cycle costs

Experience at various chlorinated solvent sites has also shown that the following objectives can be significant drivers:

- Meet commitments for expenditure of funds for environmental restoration
- Meet public expectations to make progress
- Comply with regulatory requirements
- Advance new technology

Some regulatory programs allow the use of *alternate points of compliance* for establishing cleanup goals. One of the most successful examples of this approach is the Plume Management Zone (PMZ) developed by the Texas Commission on Environmental Quality in 1999. Under this program, a site owner can establish a PMZ if certain conditions are met, such as having a shrinking or relatively stable plume in a water-bearing unit that is not used for municipal drinking water supply. Alternative points of compliance are also the basis of Superfund's Technical Impracticability (TI) waivers and the Resource Conservation and Recovery Act's (RCRA) Alternative Concentration Level (ACL) provision.

In the end, learning to value what is attainable and beneficial may be our greatest opportunity for future progress.

12. Which in situ source treatment technologies are receiving the widest use?

As of 2008, five general approaches (listed below) are being widely used for in situ treatment of chlorinated solvent source zones. Each of these approaches has one or more variants with specific advantages in specific settings. To date, all these approaches have seen tens to hundreds of full-scale applications. Overviews of these technologies can be found in SERDP (2006) and detailed evaluations of them are presented in technology-specific SERDP/ESTCP project reports available at www.ESTCP.org. Other established technologies include in situ vapor extraction, in situ air sparging, multi-phase extraction, surfactant flushing, and steam flushing.

Key attributes of current frequently used in situ source treatment technologies.

| General Approach | Variant | Key Attributes |
|-------------------------------|----------------------------------|--|
| In situ chemical oxidation | Permanganate | With a few exceptions, injection of a strong oxidant has the potential to address all chlorinated solvents. Often requires multiple applications. Not generally cost-effective for extensive DNAPL. More cases of concentration "rebound" following treatment than with other remediation technologies. Low process complexity. Delivery and complete mixing of oxidant in intended treatment zone poses the key challenge. Secondary water quality issues may need to be addressed. |
| | Peroxide | |
| | Persulfate | |
| Thermal | Conductive heating | Heaters are placed in the source zone on close-spacings and heating occurs by conduction. Temperatures in excess of water's boiling point can be achieved. This technology is generally more effective in low permeability zones than other approaches. Inflow of cold water in groundwater zones hampers effectiveness and increases cost. Vapor and liquid capture and treatment may be needed. |
| | Electrical resistive heating | Electrodes are emplaced and heating is achieved by passing current through the soil. Temperatures up to water's boiling point can be achieved. Efficacy is constrained by the uniformity of heating. Inflow of cold water in groundwater zones hampers effectiveness and increases cost. Vapor and liquid capture and treatment systems may be needed. |
| Enhanced biodegradation | High solubility substrate | Injection of highly soluble substrate such as molasses and lactate. Mixing performed by injection combined with pumping (recirculation) or, more commonly, by injection alone. Can increase concentrations of daughter products. Complete mixing of substrate in intended treatment zone poses the key challenge. |
| | Low solubility substrate | Injection of less soluble substrate such as vegetable oil, lactate polymers, mulch, etc. Typically injected via closely spaced points (vegetable oil, polymers) or, for mulch, in trenches. Can increase concentrations of daughter products. Complete mixing of substrate in intended treatment zone poses the key challenge. |
| In situ chemical reduction | Zero valent iron via injection | Macro- or nano-size iron is delivered to a targeted zone via direct injection, hydraulic fracturing, or pneumatic fracturing. Sparse distribution of distributed iron can limit effectiveness. |
| | Zero valent iron via soil mixing | Applicable to most chlorinated solvents. Soil mixing reduces or eliminates concerns about delivery of treatment material to affected zones. Combined with steam injection during auger mixing at a few locations. Only applicable to soils that can be mixed (free of rock cobbles and debris). Post treatment soil strength may be reduced. |
| Monitored natural attenuation | Source zone MNA | Often used as polishing step for weathered source zones and/or following active treatment. Requires knowledge of attenuation processes and, in most cases, temporal data demonstrating decreasing trend in source zone concentrations. May require longer time frame than engineered approaches. |

Over the past two decades, large investment by SERDP/ESTCP, other government agencies, and industry have driven the development of new technologies and vast improvements in their application. Undoubtedly, the progress of the past will continue in the future.

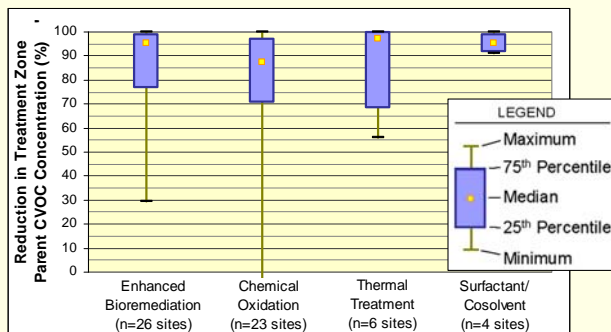
13. What can we expect from common source treatment technologies?

Kavanaugh et al. (2003), the USEPA expert panel report on the DNAPL remediation challenge, concluded that the outcomes of source depletion (remediation) projects were highly uncertain (see FAQ 16). Since then, results from several DoD-funded studies have been published regarding the performance of source treatment technologies, primarily focusing on the most commonly available performance metric—dissolved concentrations in groundwater. The following provides a brief review of these studies.

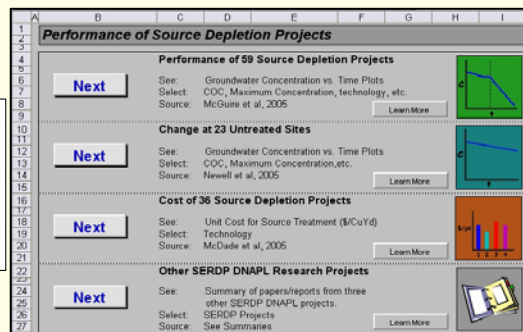
SERDP Study

A quantitative study of source depletion performance was conducted at 59 sites as part of a chlorinated solvent initiative sponsored by SERDP (McGuire et al., 2006; GSI, 2006). This study focused on a single metric: the change in groundwater *concentration* in source zones before and after one of four source depletion technologies (chemical oxidation, bioremediation, thermal treatment, and surfactant/cosolvent flushing) was applied. Forty-two of the 59 sites were described as “full-scale” projects with the remaining 17 sites as “pilot-scale” projects. The study is presented in the peer-reviewed literature (McGuire et al., 2006).

Results indicated that the median percent reduction in parent chlorinated compound concentrations due to treatment was 92%. The median reduction in parent compound concentrations for each technology were bioremediation, 95% (n=26); chemical oxidation, 88% (n=23); thermal, 97% (n=6); and surfactant/cosolvent, 95% (n=4) (see figure below). Concentration *rebound* (an increase in groundwater concentrations from a post-remediation low) was most prevalent at sites where chemical oxidation was applied, a pattern also found in the other studies discussed below. Based on the available site characterization data, none of the 59 source depletion projects were able to meet drinking water standards throughout the entire treatment zone.



Reduction in Parent Chlorinated Solvent Concentration in Treatment Zone After Treatment Groundwater (McGuire et al., 2006)



Screen Shot from Source Depletion Decision Support System (GSI, 2006)

Although the median remediation project seemed able to reduce source zone groundwater concentrations by a full order of magnitude (i.e., a 90% reduction), in some cases, particularly for thermal treatment, concentrations were reduced by two orders of magnitude (i.e., a 99% reduction). Also, it is important to note that most of the treatment projects were relatively small in size. The median treatment volume was equivalent to a chlorinated solvent source zone only 100 feet by 100 feet by 15-feet thick (~5,000 cubic yards). The median distance between a treatment point (an injection point or thermal point) and the monitoring wells where the data were collected was only 7 feet.

When the cost of source treatment is considered (see FAQ 14), it becomes apparent that in situ treatment is much more practical to apply to “room-scale” chlorinated solvent source zones (i.e., treatment zones that are a few thousand cubic yards in size). For “city-block-scale” and larger source zones (treatment zones that are hundreds of thousands or millions of cubic yards), the cost of source zone treatment may be prohibitive.

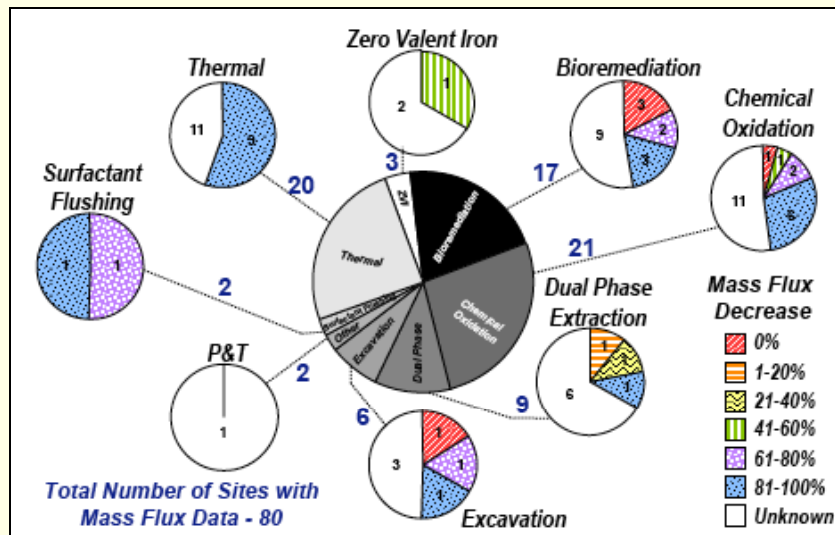
ESTCP Data Mining Projects

The DNAPL Technology Evaluation Screening Tool (Lebrón et al., 2008) used a simpler method than the SERDP study to determine the reduction in groundwater concentrations but obtained similar results. The median percent reduction in concentration achieved in 72 treatment projects was 92%. Individual technologies were reported as having the following median concentration reductions due to treatment: bioremediation, 95% (n=17); chemical oxidation, ~91% (n=40); and resistive heating, 91% (n=10).

Two other ESTCP data mining studies focused on individual remediation technologies. Performance data from 53 chemical oxidation projects showed a median reduction in treatment zone dissolved phase concentrations for TCE of 66% (Krembs, 2008). At 14 thermal treatments, the treatment zone dissolved phase concentrations were reduced by about one order of magnitude (90%) or less for 9 of the treatments, and the reduction was equal to or greater than two orders of magnitude (99%) for 4 treatments. The mass flux reduction was estimated to be an order of magnitude or less at half of the treatments and equal to or greater than two orders of magnitude at the other half of the treatments (Kingston, 2008).

U.S. Navy Study

The U.S. Navy performed a technical survey of DNAPL treatment performance at over 80 sites (Geosyntec, 2004). Half of the respondents (vendors, users, and regulators) claimed that the use of a source depletion technology for DNAPL was "successful," though measures of "success" varied. Thermal technologies and chemical oxidation with permanganate were the most widely used technologies. The U.S. Navy developed a graphical summary of *mass flux decrease* (shown below) and source mass removal (not shown) in "DNAPL Management Overview" (NAVFAC, 2007). Note that of 80 total DNAPL treatment attempts, 31 were full-scale applications and 49 were pilot tests.



Summary of source mass flux decrease sorted by technology
(NAVFAC, 2007; based on data from Geosyntec, 2004)

The Navy (NAVFAC, 2007) concluded that:

- Only partial DNAPL mass removal or destruction can be achieved, although that may be sufficient to meet overall management objectives at some sites (e.g., small, shallow sources in permeable media).
- Cleanup standards based on state and federal MCLs are "extremely unlikely to be met".

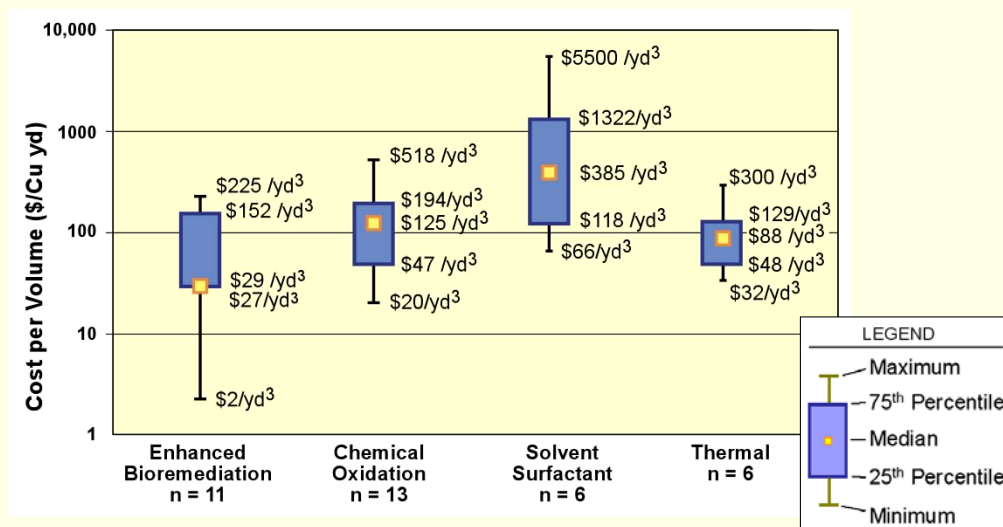
The results from this Navy study were obtained by asking site personnel to report the mass removal that was achieved by each project, while the other studies were based on mining monitoring data from sites and performing an independent analysis of treatment technology performance.

Rule of Thumb: Based on the results of the studies described above, well-implemented in situ remediation projects are likely to reduce source zone groundwater concentrations by about *one to possibly two orders of magnitude* (90 - 99% reduction) from pretreatment levels. However, it is difficult to predict the actual performance of an individual remediation project prior to its application in the field. Treatment trains (successive applications of different technologies) may be one approach to reducing concentrations beyond what a single treatment episode can achieve.

14. How much does it cost to treat source zones?

A number of studies have evaluated the cost of source depletion technologies (e.g., McDade et al., 2005). These efforts suggest the general rule of thumb that most engineered in situ treatment technologies will cost in the range of \$30 to \$150 per cubic yard of treatment volume. Assuming a 20-foot thick treatment zone, area costs will range between \$1 million and \$5 million per acre. The broad range in cost reflects use of different technologies, specific site conditions, and different endpoints.

One recent study of source depletion costs for source zone treatment at 36 field sites was performed by compiling unit costs for four different technologies in dollars per cubic yard (McDade et al., 2005). While some approaches, such as thermal treatment, have some nonlinear elements in the cost-to-volume relationship that creates inaccuracies in using unit costs (e.g., large mobilization cost that increases the unit cost for smaller sites), in general the costs connected to all the technologies are highly correlated to treatment volume. Results from this study are shown below:



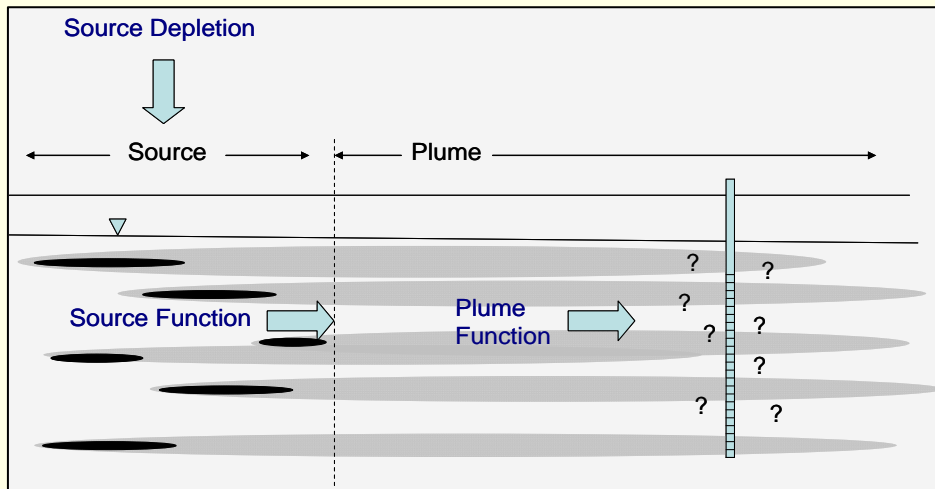
Unit costs of source zone treatment (McDade et al., 2005)

Note that these data represent broad, planning-level remediation costs. Actual remediation costs are dependent on a variety of site-specific geologic, chemical, safety, and access issues, as well as regulatory requirements and various other conditions. While treatment volume is an important cost driver, other factors can dramatically increase engineered in situ remediation costs, such as: i) source zone in fractured rock; ii) the presence of surface obstructions such as buildings, runways, pipelines, etc.; iii) deep source zones; and iv) low permeability source zones. Another factor that can drive up costs is when multiple sources are distributed over large but contiguous work zones, creating a large, dilute plume that is very difficult to manage.

Rule of Thumb: By combining FAQs 13 and 14, it appears that investments on the order of millions of dollars per acre can potentially achieve reductions of one or two orders of magnitude in chlorinated solvent mass and concentration in source zones. Note that this observation is very general. Without doubt, there are exceptions that could involve higher or lower costs and greater or lesser amounts of contaminant depletion. Furthermore, new and improved technologies hold the potential of better performance and/or lower cost. Finally, there are other reasons to conduct source treatment in addition to reducing source zone concentrations (see FAQ 21 for more information).

15. How will reduced loading from sources affect plumes?

Most remedial actions are driven by potential risks associated with exposure to contaminants in plumes (vapor or groundwater). Given this, evaluation of any remedial measure often involves two questions. The first is how the measure will reduce contaminant loading to the downgradient plume (source function) over time. The second is how a reduction in loading to the downgradient plume will affect downgradient concentrations at points of exposure over time (plume function). These concepts are presented in the figure below.



Conceptualization of the relationship between source depletion, modified contaminant loading from the source, plume response to reduced loading from the source, and downgradient reductions in exposure at a well

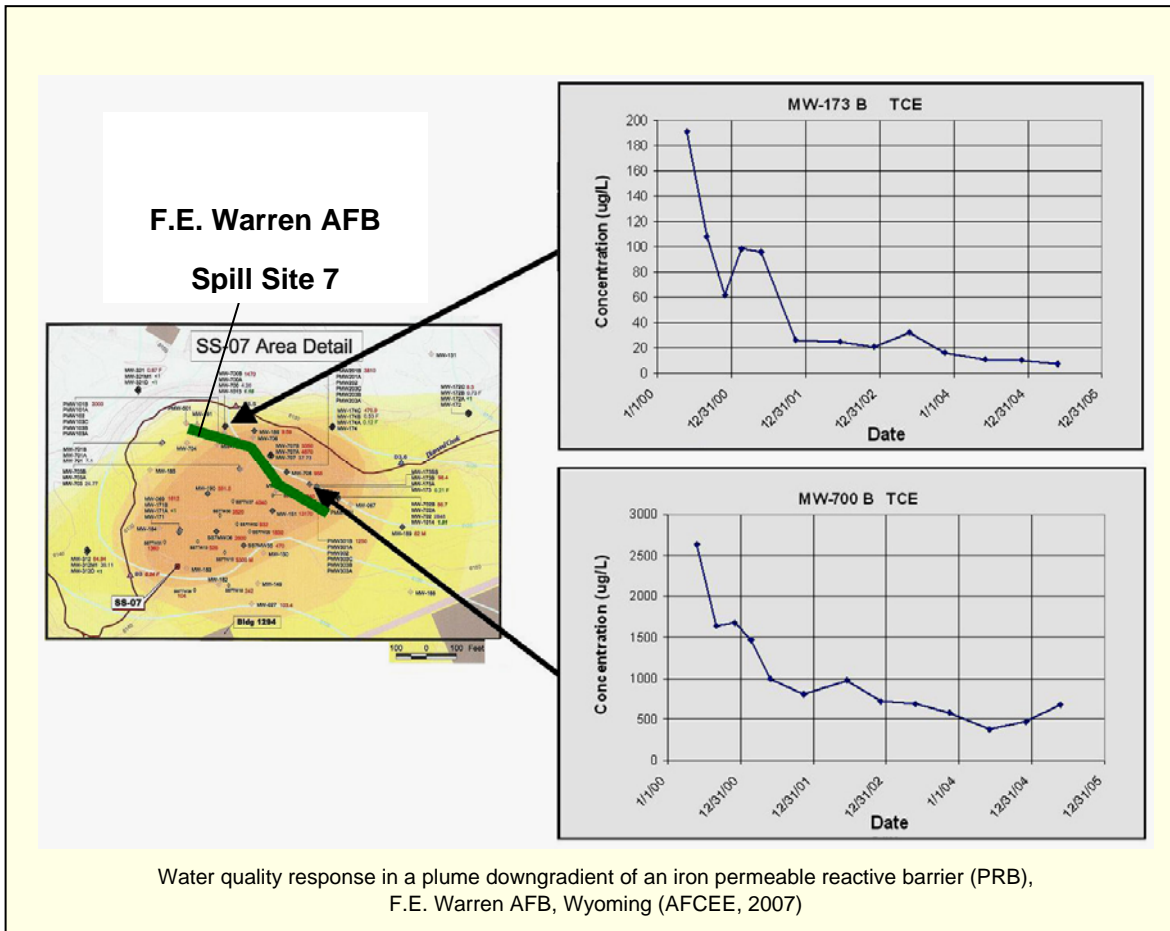
One example of the difficulty in cleaning up the downgradient plume is illustrated by the results from the zero valent iron permeable reactive barrier (PRB) installed in 2000 at F.E. Warren Air Force Base (AFB), Wyoming (AFCEE, 2007). The PRB produced a near-zero chlorinated solvent load to the downgradient groundwater plume (analogous to complete source containment or removal) in this heterogeneous aquifer. Monitoring wells MW173B and MW700B (located 12 and 18 meters downgradient of the PRB) indicated a one order of magnitude improvement in water quality after 5 years (see figure on following page).

Given an estimated seepage velocity of 1 ft/day, the persistent dissolved-phase concentration can be attributed to release of sorbed solvents in transmissive zones and back-diffusion of dissolved and sorbed contaminants stored in low permeability zones. It appears from extrapolation of the water quality data that the concentrations downgradient of the PRB will persist for an extended period. A low permeability inclusion in a core from F.E. Warren AFB is shown on the right. Clearly, slow diffusion of contaminants stored in this material could serve as a long-term "secondary source" within the plume, although the total flux may be much less than from a DNAPL source zone.

It is important to note that, although the PRB has not achieved MCLs immediately downgradient of the barrier, it has met its intended purpose of attaining MCLs in a downgradient stream, partly due to mixing with surface water. Further, it has been suggested that natural attenuation within the plume may adequately control the risks posed by back-diffusion of stored contaminants.



Low permeability layer in a soil core from F.E. Warren AFB



Another example is a chlorinated ethene release site at Kings Bay, Georgia (Chapelle et al., 2004). There, a series of in situ oxidation source-removal actions was initiated in late 1998, resulting in source-area PCE concentrations being lowered from the 4,000 to 5,000 µg/L range to <100 µg/L. After 2 years, a one order of magnitude reduction in total chlorinated ethene concentration was observed 160 feet downgradient of the treatment zone. Again, this remedial action did not reach MCLs in the target treatment zone, but it was successful in achieving a number of less aggressive goals.

The USEPA-sponsored REMChlor model (USEPA, 2007; Falta et al., 2005a, 2005b) is a recently released analytical model that can simulate partial source depletion any time after the release occurs, and shows the subsequent response of the plume. It will likely prove to be a powerful tool to evaluate the impact of source zone remediation and post-remediation plume management requirements. In addition, other investigators are working on new mathematical models that describe source and plume functions, and models that capture matrix diffusion effects are just now emerging. We hope that these efforts will lead to tools that can be used to conduct a priori predictions of how specific actions will change downgradient concentrations in dissolved plumes. In the meantime, one of the best tools is the empirical knowledge that can be derived from experiences at field sites.

Rule of Thumb: Reductions in the upgradient sourcing of plumes of about one order of magnitude or more often yield at least a one order of magnitude improvement in downgradient groundwater quality. In instances of fast groundwater flow, low mass storage in plumes, and/or active contaminant attenuation in plumes, a two to three order of magnitude downgradient improvement in water quality may be observed over a period of several years.

16. What are the effects of source treatment on cleanup time frames?

One benefit of active source treatment is that it will take less time for a site to reach its cleanup goals. However, it is difficult to quantify exactly how much time will be saved. Kavanaugh et al., (2003) concluded that quantitative predictions of the potential benefits and adverse impacts of chlorinated solvent source depletion actions are "...highly uncertain. These uncertainties remain as significant barriers to more widespread use of source depletion options."

A recent SERDP study (Newell and Adamson, 2005; GSI, 2006; Newell et al., 2006) utilized simple planning-level relationships to evaluate how quickly source zones might clean up with and without active source treatment. As noted in FAQ 13, active treatment generally leaves some contaminant mass behind. The study concluded that there may be some theoretical cases where there will be "equal benefit for equal work" (i.e., where the percent reduction in cleanup time frame will equal the percent reduction in source mass). However, this outcome is unlikely at most sites due to concentration "tailing" caused by factors such as DNAPL dissolution from less permeable zones, back-diffusion of stored contaminants, and slow desorption effects (see FAQs 3 and 8).

To simulate this tailing effect, the study presented a *first order decay model* for the source with decreasing concentrations over time, but decreasing at a slower rate as concentrations get lower and lower. This is the same source function that is used in the USEPA's REMChlor model when the source response variable (called "gamma") is set to the middle of the recommended range. The REMChlor example presented below shows the effect of the tailing on cleanup time frames at a hypothetical site, where removal of 90% of the source mass reduced the remediation time by only 22%. Other source zone models presented in the SERDP study (and available in the REMChlor model) can simulate a variety of source responses, such as a constant or near-constant source zone concentration followed by tailing concentrations; fast initial concentration reductions, followed by extensive tailing; or concentration that declines at a linear rate (in which the mass is completely depleted in a relatively short time).

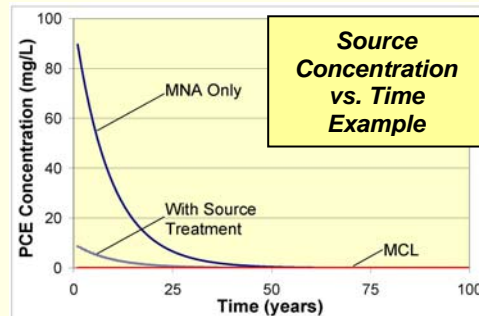
Both the SERDP study's design charts and the USEPA's REMChlor model can be used to show the theoretical reduction in the cleanup time frame for different starting conditions, mass removals, and remediation endpoints. These tools are conceptual in nature, rely on several simplifying assumptions, and have not been fully verified against field data. Nevertheless, they provide a planning-level picture of the way that source zones may respond to active treatment when the critical tailing effect is considered.

EXAMPLE OF TIME FRAME ANALYSIS USING REMChlor:

Tutorial 6 built into the REMChlor model was used except with a smaller source mass of 275 kg. Other key variables include a starting concentration of 100 mg/L of PCE, an initial mass flux leaving the source of 30 kg/yr, and a middle-range value for the source response function (gamma = 1.0). The following source cleanup times were predicted:

- No source treatment: **95 years** to reach 0.005 mg/L
- Remove 90% of source mass: **74 years** to reach 0.005 mg/L

Although not all projects will have this same result, this hypothetical example using REMChlor illustrates how tailing can impact the source cleanup time frames.



Several software packages are available to help estimate source longevity:

- **SourceDK** (Farhat et al., 2004). Develops linear extrapolation from temporal data and/or applies simple first order decay relationship to MNA source zones.
- **BioBalance** (Kamath et al., 2006). Simulates changes in mass flux and/or mass on remediation time frame; considers sustainability of chlorinated solvent source zone.
- **Natural Attenuation Software** (Widdowson et al., 2005; Chapelle et al., 2003). Simulates NAPL dissolution and effect of remediation on plume cleanup; shows plume response (ESTCP project).
- **REMChlor** (USEPA, 2007; Falta et al., 2005a, 2005b). Incorporates a power function to evaluate the effect of remediation on source longevity and plume response.

Source decay models are designed to show the potential impact of tailing effects on a single remediation metric: the reduction in cleanup time frame. Note that there are other benefits that accrue from active source treatment in addition to the reduction in the cleanup time frame (see FAQ 21 for more information).

17. Which containment measures are receiving the widest use?

Containment is a relatively common management approach for source zones, and in particular, it has been the primary approach for large releases. Kavanaugh et al. (2003) concluded that “at the majority of DNAPL sites, containment of the source zone and/or management of the dissolved plume...have been the dominant strategies of choice.” The alternatives to active source depletion include containment, long-term source management via MNA, and/or institutional controls. These management strategies focus primarily on reducing concentrations in the plumes rather than in the source zones.

Key attributes of containment technologies

| Approach | Variant | Key Attributes |
|-------------------------------|--|--|
| Hydraulic containment | Pumping wells | Groundwater leaving source zones (DNAPL, sorbed contaminants, low permeability zones) is captured using pumping wells. Water is treated above ground and either discharged to surface water or reinjected. Reliable, proven technology but with relatively high life-cycle costs. |
| Permeable reactive barriers | Iron barriers | Trenches are filled with sand/gravel and metallic iron. The resulting abiotic reaction reduces the mass flux of solvents leaving the trench. Perceived to be a reliable technology, with operational lifetime of 15 years or more. Costs have increased in recent years due to higher iron costs. |
| | Sparge barriers | A line of air sparging wells, a horizontal sparge well, or a sparge trench is installed to intercept and volatilize contaminants from the dissolved plume. Exposure to vapors sometimes an issue. |
| | Biodegradation barriers | Trenches are filled with biologically active material (such as mulch) that creates anaerobic condition amenable to biodegradation via reductive dechlorination. Based on one project, mulch walls will likely have lower treatment effectiveness but lower cost than a zero valent iron barrier. |
| Physical containment | Slurry walls (often combined with pumping) | Vertical barriers are constructed using standard geotechnical technologies such as bentonite slurry walls or jet grouting. The resulting barriers have very low hydraulic conductivity (10^{-7} cm/sec or lower) if installed correctly. Considered a proven technology. Sensitive to surface obstructions. May require bottom clay for keying in the wall. |
| | Caps | Horizontal barriers can be constructed in a variety of ways to divert rain and prevent the generation of leachate from vadose zone sources. |
| Monitored natural attenuation | MNA for treatment of downgradient plume | Studies are performed on concentration trends with time and distance, geochemical conditions, etc. to determine if naturally occurring processes (dispersion, biodegradation) are containing the migration of the plume. Frequently used approach that has numerous tools available to help site managers evaluate MNA (Wiedemeier et al., 1999). |

18. What can we expect from containment measures?

Hydraulic Containment

When active source remediation is not used, hydraulic containment via groundwater pump-and-treat is the most common remedial technology. It is considered a proven technology for managing source zones. Many site managers are reluctant to install pump-and-treat systems due to high life-cycle costs and the perception that the systems will be operated indefinitely. Recently, both site managers and the USEPA have investigated methods to optimize pump-and-treat systems to make these systems more efficient over the long term without compromising the effectiveness of the containment system. Note that hydraulic containment is often combined with physical containment in some source zones.

Permeable Reactive Barriers (PRBs)

A PRB technology firm evaluated 52 full-scale zero valent iron PRB applications and concluded that 43 of them are meeting regulatory objectives, even though at least six of the 43 exhibit deviations from predicted flow fields (RTDF, 2003). Hydraulic issues were to blame for the deficiencies at the other nine sites. As of 2003, there was no indication that precipitation problems reduce iron reactivity to the degree that iron rejuvenation or replacement is required, and it appeared likely that most iron PRBs will function for at least 10 to 15 years without requiring refurbishment. At least one site (F.E. Warren AFB) appears to have a problem with back-diffusion that is preventing the PRB system from achieving MCLs downgradient of the barrier. Based on a limited sample of installations, mulch walls can be significantly cheaper but appear to have lower treatment efficiency than zero valent iron walls.

Physical Containment

The USEPA evaluated the performance of subsurface engineered barriers (e.g., physical barriers) in 1998 by making detailed assessments of 36 sites with vertical barriers. It concluded that if properly designed, such barriers are effective containment systems for the short and middle term, where "middle term" refers to a period of less than 10 years. At four of the 36 sites, leaks were detected at the interface between the barrier and anchor materials (i.e., barrier key) but were all repaired "with relative ease." Overall, a total of four out of the 36 sites were determined to have "less than acceptable" performance, and seven sites had insufficient data to make an evaluation. It should also be noted that there are few data from sites that are 20 years old or older, so long-term results are uncertain.

Monitored Natural Attenuation

MNA is another commonly accepted approach for managing plumes from chlorinated solvent source zones. A study of 191 chlorinated solvent sites (source zone plus plume) where MNA was considered as a remediation alternative showed that MNA was implemented as the sole remediation remedy at 30% of the sites, MNA in conjunction with some type of active treatment at 47% of the sites, and MNA was determined infeasible at 23% of the sites (McGuire et al., 2004). Key reasons for excluding MNA from further consideration were the presence of expanding plumes and/or unreasonably long projected cleanup time frames. Biodegradation was reported to be the most important MNA process at 70% of the sites.

MNA was accepted as the remedy for a wide variety of site conditions. At 45 sites where MNA was being applied, 40% had maximum site concentrations greater than 10 mg/L. The median groundwater seepage velocity at these sites was about 50 ft/yr.

19. How much does containment cost?

Hydraulic containment, PRBs, and physical barriers are proven technologies with well-developed cost information. Some very general rules of thumb used by practitioners include:

- Large site pump-and-treat systems (multiple contaminants, ~100 gallons per minute [gpm]): Median capital cost: \$2 million. Median operations and maintenance cost: \$260,000 per year.
- Small site pump-and-treat system (VOCs, ~20 gpm): Median capital cost: \$300,000. Median O&M cost: \$40,000 per year.
- Slurry wall barriers: \$3-\$10 per square foot for barriers up to 50 ft deep (see photo below). This type of wall can convert a large pump-and-treat system into a small pump-and-treat system at some sites.
- PRBs using zero valent iron: Median cost: \$4,500 per linear foot for iron barriers up to 45 ft deep.
- PRBs using mulch: \$400 per linear foot (based on one installation with no-cost mulch supply (see photo below).
- MNA studies include up-front costs between \$50,000 and \$200,000 (accounting for increased sampling, more detailed data analysis, and in some cases computer modeling). The long-term costs (primarily for monitoring) depend on the number of wells, the sampling frequency and methods, and the analyses needed.

These rules of thumb for expenses do not include all costs of implementing these technologies, and site-specific conditions will clearly affect these numbers. They simply provide a starting point.

SOURCES: USEPA (2001); Gavaskar et al., (2000); USEPA (2002); authors' experience.



Construction of a bentonite slurry wall vertical barrier

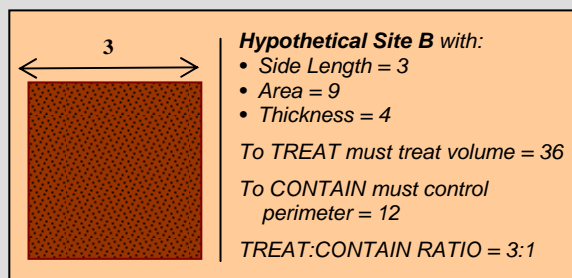
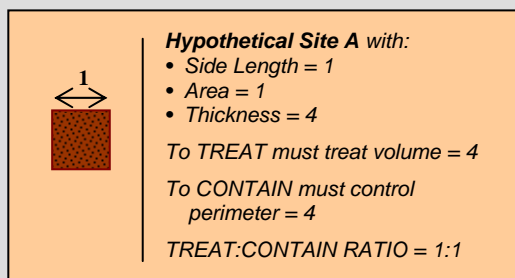


Construction of mulch-filled PRB

20. How does one compare treatment versus containment?

One of the key questions faced by site managers is whether it is better to treat or to contain a chlorinated solvent source zone. Some key considerations used for resolving the merits of source depletion versus containment are discussed below:

- **Size Matters.** The size and architecture of the source zone strongly affect the economic comparison of treatment versus containment alternatives (see figure below).
- **Time Matters.** Ensuring containment effectiveness over decades, or even centuries, is very difficult, and often partial treatment is understandably preferred if only to reduce the burden on future generations. Conversely, at many sites it takes considerable time to observe the benefits of source depletion throughout the plume's entire length. Many plumes have hydraulic residence times (the time it takes one pore volume to flush through the entire plume) of 10-40 years, and much more than one pore volume may be required to realize the benefits of source depletion (see Falta et al., 2005a, 2005b).
- **Intangibles Matter.** While cost is an important consideration, it has been the authors' experience that cost is only one of many factors that drive remedial strategy decisions. In many cases, the need to comply with regulatory or public concerns may be more pressing than cost. In other cases, future land uses may make some containment more acceptable.
- **Economic Models Matter.** The timing of expenditures, and the methods of comparing future and present costs, are difficult and contentious issues. Typically, source treatment is capital intensive, with higher initial costs, but containment generally has higher long-term costs (for monitoring and replacements). Consequently, comparisons are sensitive to if and how future costs are discounted. For example, an annual \$100,000 cost over 30 years represents \$3 million if no discounting is used, but a net present value (NPV) approach may indicate that this liability can be completely funded by an upfront cost of only \$2 million. But this cost analysis is also sensitive to the discount rate used. The U.S. government currently uses a 3% discount rate (Office of Management and Budget, 1992, 2006), but many corporations use a much higher rate of return for NPV calculations. And of course, for many chlorinated solvent releases, costs may still have to be paid each year long after the first 30 years.
- **Multiple Treatments May Be Needed.** Before application, it is often difficult to predict what effect the source treatment will have, what fraction of the mass can be removed, what residual concentrations will be observed, and what reduction in mass flux can be expected. Although modeling and treatability or pilot studies can reduce this uncertainty, it cannot be eliminated. Using treatment trains (two or more different technologies applied in succession) is one promising approach to reducing source strength to the point where post-treatment care is no longer needed. However, the need for and nature of the appropriate follow-up treatment technology may not be known until after the first treatment.
- **Consider Natural Attenuation Capacity.** One of the most important benefits of source depletion can be to reduce the source strength to the point that MNA can be used to manage the remaining source and plume. Source depletion technologies should not permanently destroy the potential for MNA, but they may delay it or reduce its efficacy, thereby increasing the life-cycle management costs.



Effect of Source Size: Source treatment capital costs typically increase linearly with source *volume*, while source containment capital costs typically increase linearly with source *perimeter*. Therefore, as source zones get larger, source treatment capital costs increase faster than containment capital costs. This is one reason why most source treatment projects are performed at smaller sites (the median treatment size from one multi-site study was ~ 5000 cubic yards; GSI, 2006), while very large sites more often employ containment strategies (see hypothetical example above for effect of source size on treatment versus containment).

21. How do site characteristics affect cleanup decisions?

The USEPA convened an Expert Panel (Kavanaugh et al., 2003) to evaluate the decision-making behind choosing between source depletion and source containment. The Expert Panel concluded that:

“the decision to implement source-zone depletion technologies for DNAPL site remediation is a highly site-specific decision, and that numerous regulatory, technical and stakeholder factors must be considered. The current decision process as practiced in the U.S., has generally resulted in selection of containment over source depletion, although as noted elsewhere there is a growing number of DNAPL sites where source depletion technologies are being deployed...The Panel concluded, however, that new approaches to this decision process are needed.”

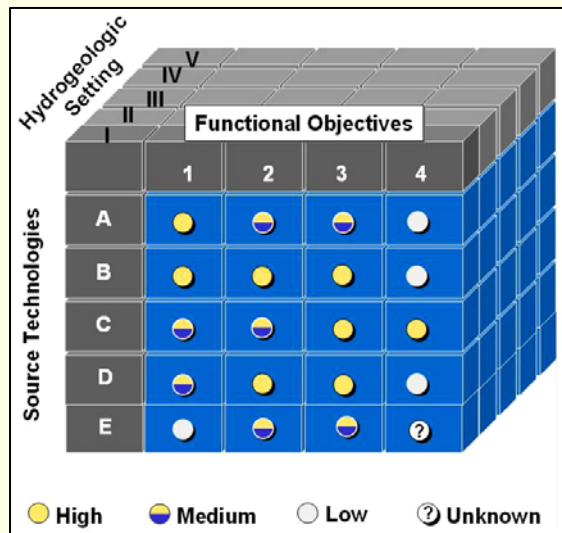
National Research Council “Cube” (NRC, 2005)

The National Research Council's *Contaminants in the Subsurface* Report (NRC, 2005) developed a multi-dimensional screening approach based on the “cube” (shown below). While the details of the cube cannot be presented here, the cube construction includes objectives, remediation technologies, and site characteristics/hydrogeologic settings such as:

- I. Granular Media with Mild Heterogeneity and Moderate to High Permeability
- II. Granular Media with Mild Heterogeneity and Low Permeability
- III. Granular Media with Moderate to High Heterogeneity
- IV. Fracture Media with Low Matrix Porosity
- V. Fracture Media with High Matrix Porosity

The NRC document uses charts relating objectives, technologies, and hydrogeologic settings to illustrate the importance of site characteristics. For example, the presence of fractured rock with high matrix porosity (such as sedimentary rock) at a site can reduce the potential effectiveness of most in situ source treatment technologies as compared to their effectiveness in granular media.

The NRC cube approach makes an important distinction between *absolute objectives* (objectives that are important in themselves) and *functional objectives* (a means to get to absolute objectives). See FAQ 23 for more information about this distinction.



The NRC “Cube.” A, B, C, etc. represent 12 source treatment/containment technologies. 1, 2, 3, etc. represent 5 cleanup objectives. In all, the NRC cube considers 300 different combinations of site conditions, source technologies, and cleanup objectives

USEPA Expert Panel Qualitative Decision Guide (Kavanaugh et al., 2003)

One of the tools developed by the Expert Panel and modified for this document is presented on the next page. It uses a “weight-of-evidence” to resolve the relative need for source treatment. Primary reasons for considering source treatment include reducing the potential for DNAPL migration, decreasing source longevity, reducing loading to downgradient plumes, attainment of MCLs, complying with regulations, and achieving intangible benefits.

**Decision Chart: Relative merits of source depletion
(adapted from Kavanaugh et al., 2003)**

How to use this chart: Circle one choice “a”, “b”, or “c” for each of the 11 rows. Add the total number of selections in each column to determine the weight of evidence for “More Need for Source Treatment,” “Less Need for Source Treatment,” or “Neutral.”

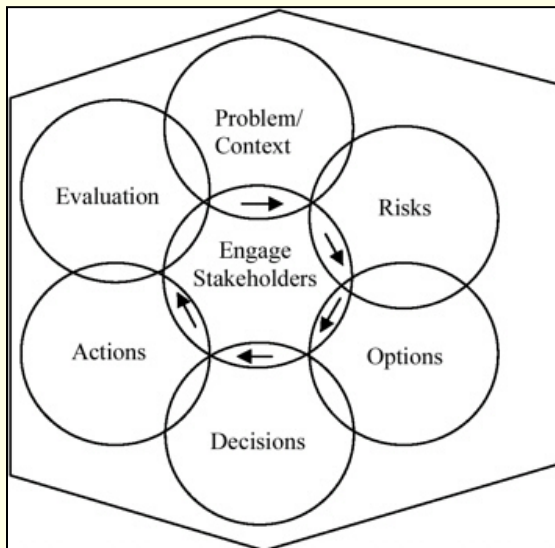
| WHY TREAT? | MORE NEED FOR SOURCE TREATMENT | NEUTRAL | LESS NEED FOR SOURCE TREATMENT |
|--|---|--|--|
| <i>Reduce potential for DNAPL migration as separate phase</i> | 1a. Expanding mobile DNAPL zone (probably rare at chlorinated solvent sites) | 1b. Free-phase DNAPL present but stable in stratigraphic traps | 1c. Immobile, residual DNAPL zone |
| <i>Reduce source longevity and long-term management requirements</i> | 2a. High life-cycle containment cost (for example, containment NPV >> cost of remediation) | 2b. Moderate life-cycle containment cost | 2c. Low life-cycle containment cost (for example, containment NPV << cost of remediation) |
| | 3a. Low reliability of containment system | 3b. Moderate reliability of containment system | 3c. High reliability of containment system |
| | 4a. High resource value that cannot be used due to DNAPL (for example, sole-source aquifer) | 4b. Moderate resource value | 4c. Low resource value (for example groundwater with high Total Dissolved Solids) |
| | 5a. High probability of a meaningful reduction in time to reach MCLs (for example, small sites with low complexity) | 5b. Moderate probability of a meaningful reduction in time to reach MCLs | 5c. Low probability of meaningful reduction in time to reach MCLs (for example, large releases at complex sites) |
| | 6a. Relatively low cost (less than ~\$1,000,000) | 6b. Moderate cost (~\$1,000,000 to \$10,000,000) | 6c. Relatively high cost (more than ~\$10,000,000) |
| <i>Reduce mass flux (reduced loading to downgradient plumes)</i> | 7a. Expanding dissolved phase plume (source loading > assimilative capacity) | 7b. Stable dissolved phase plume (source loading ~ assimilative capacity) | 7c. Shrinking dissolved phase plume (source loading < assimilative capacity) |
| | 8a. Receptor impacted or will be impacted soon (for example, < 2 years travel time) | 8b. Potential long-term risk to receptor (for example, >2 years travel time) | 8c. No risk to receptors now or in the future |
| <i>Near-term attainment of MCLs</i> | 9a. Need for rapid cleanup (e.g., impending property transfer) | 9b. Limited need for rapid cleanup | 9c. Resources not in use during the expected time frame for restoration of aquifer and no other exposure pathways likely (e.g., vapor migration) |
| <i>Regulatory requirement</i> | 10a. Clear regulatory driver requiring source cleanup | 10b. Regulators open to consideration of both treatment and containment approaches | 10c. Little or no regulatory pressure for aggressive treatment |
| <i>Intangibles</i> | 11a. Desire for active remedy; desire to test new technologies; desire to reduce stewardship burden on future generations; clear public preference for source treatment | 11b. Neutral on intangible issues | 11c. Desire for low-impact remedy; desire to use proven technologies; desire to not expend financial resources for limited risk reduction benefits; few or no public perception issues |

22. Taking stock: In retrospect, why have we not been more successful?

Many fields, including civil and geotechnical engineering, teach this admirable notion: If something fails, learn from the experience and avoid repeating it. Unfortunately, the authors have observed situations where stakeholders appear to get caught in a cycle of remediation attempts that result in little forward progress. Some of the reasons for this impasse included:

- Poorly designed and misapplied technologies.
- Poor understanding of what technologies can and will do.
- Misunderstanding the extent and/or distribution of contaminants in source zones and/or misunderstanding the technical limits regarding how accurately or completely a source zone can be characterized.
- Poor recognition of uncertainties inherent in remedial system design and failure to learn from system performance monitoring data to optimize the cleanup approach.
- Stating remedial objectives that can only be achieved over long periods of time (i.e., satisfying drinking water standards everywhere), without using other short-term objectives that can be tied to remedial system design and optimization.

One approach to improving cleanups is described in the Presidential-Congressional Commission on Risk Assessment and Risk Management, which emphasizes *adaptive site management*. Engaging stakeholders throughout the process is important for adaptive site management, as is the iterative process of constant evaluation and optimization. Adapted from: National Research Council (2003) – Environmental Cleanup at Navy Facilities: Adaptive Site Management.



Schematic illustration of adaptive site management as advanced in Environmental Cleanup at Navy Facilities (National Research Council, 2003.)

23. How can we set cleanup objectives that are attainable and beneficial?

The authors observe that unattainable near-term objectives are often established for chlorinated solvent spill site cleanups (i.e., achievement of MCLs in source zones or throughout the site), and that this then leads to misapplications of technology, inappropriate monitoring plans, misinterpretation of results, frustration between the parties involved, and unnecessary expense.

Cleanup objectives can generally be classified into two different categories:

- Absolute objectives are objectives that are important in themselves, such as “protect human health and the environment.”
- Functional objectives are a “means to achieve the absolute objectives” and include containing plumes, reducing concentrations and mass flux, managing risks, reducing mass, and potentially decreasing plume longevity.

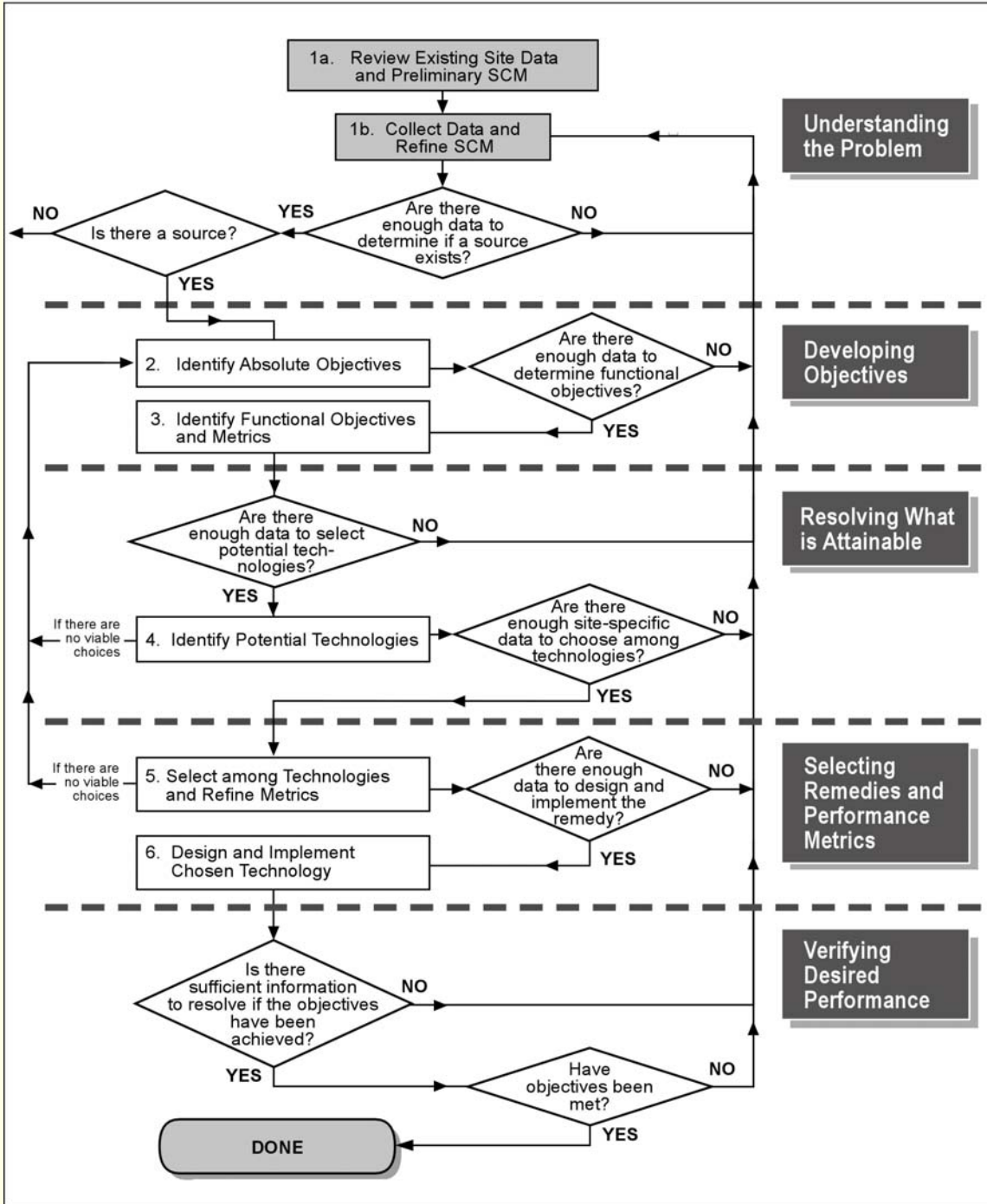
The USEPA’s Expert Panel (Kavanaugh et al., 2003) concluded that, although a drinking water quality goal is either implicitly or explicitly prescribed in most state and federal environmental laws, “this goal is not likely to be achieved within a reasonable time frame in source zones at the vast majority of DNAPL sites.” The panel noted that:

In recent years, there has been a trend towards the adoption of a more pragmatic regulatory approach by some regulatory agencies that are considering alternate or intermediate performance goals and phased remedial action approaches, for cleanup of contaminated sites. Such flexibility may result in implementing alternative strategies for groundwater cleanup, including: (1) establishment of management zones where cleanup goals other than drinking water standards may be applied, (2) groundwater classification schemes that permit alternative remedial action goals, and (3) other flexible regulatory approaches that do not impose non-degradation requirements or drinking water standards in DNAPL source zones. These new federal and state regulatory policies provide a more encouraging climate for implementation of innovative source-depletion technologies, in those situations where partial depletion of DNAPL sources is deemed an intermediate goal as a part of phased site cleanup.

The potential for success can be greatly enhanced by establishing both absolute and functional objectives (NRC, 2005). Absolute objectives should be regarded as long-term goals and the functional objectives as shorter term operational goals that ideally lead to meeting the longer term absolute objective. In most regulatory guidance, drinking water standards or background levels are *de facto* absolute objectives, although alternate levels can sometimes be set after considering beneficial resource use and risk. See FAQ 10 for more thoughts on goals.

It is important to recognize that the path to cleanup is rarely linear and is more frequently iterative as we continue to learn more about sites through each new observation and data point. This is one reason that the U.S. Navy and others have stressed the use of flexible Records of Decision to foster the use of technologies appropriate for conditions as they change over time (Battelle, 2004). To help formalize an effective decision-making process for remediating sites, the U.S. Army charged the National Research Council to develop a decision process, which is shown on the next page (NRC, 2005). Its primary relevance is to impose discipline in defining objectives that are beneficial, attainable, and verifiable.

MAKING DECISIONS



Remediation Decision Process (adapted from NRC, 2005).
SCM = site conceptual model.

24. How can we be more successful at site cleanup?

Given what we now know (including FAQs 1-23), we can be more successful in the future than we have been in the past. Building on this, the following is offered for consideration:

1. Establish *absolute* objectives for each project (i.e., drinking water standards as cleanup levels), but recognize that these will be long-term goals at most sites (see FAQ 22 for a discussion of absolute versus functional objectives).
2. Have an up-to-date understanding of what can be practicably achieved by available technology, and communicate your experiences so that others can gain from your insights.
3. Develop shorter term *functional* objectives to confirm progress towards the absolute objectives. Select these in such a way that progress towards cleanup is measurable and acknowledged, and optimization of cleanup systems is encouraged.
4. Recognize uncertainties in site characterization and system performance projections, and design a remedial strategy that is updated as new observations and data are recorded (see “The Observational Approach” below). The USEPA’s Triad approach embodies many of the principles of the observational approach (www.triadcentral.org).
5. Use adaptive management practices, including use of flexible Records of Decision, treatment trains if needed, and constant optimization of remedial systems and monitoring networks.
6. When source containment is the chosen remedial strategy, clearly communicate the long-term nature of this to all stakeholders.
7. When source treatment is chosen as a part of the remedial strategy, clearly communicate the uncertainties associated with the outcome to all stakeholders. Develop a long-term strategy that incorporates the need for possible follow-up treatment and/or containment, and clearly communicate this to all stakeholders as well.
8. Accept that remedial actions may not lead to achievement of cleanup objectives and learn from these experiences rather than simply viewing them as failures.

The Observational Approach

One method for managing the uncertainty at chlorinated solvent sites is the Observational Approach, developed for geotechnical engineering by Terzaghi and Peck (1948). This approach consists of the following steps (Peck, 1969; NRC, 2006):

- Assess probable conditions and develop contingency plans for adverse outcomes.
- Establish key parameters for observation.
- Measure observational parameters and compare to calculations.
- Compare predicted and measured parameters.
- Change the design as needed.

These same concepts are embodied in the USEPA Triad Approach (ITRC, 2003a; Crumblin, 2004), a process for characterizing and remediating contaminated sites by managing decision uncertainty.

25. Where can I find more information?

Some key resources for more information about chlorinated solvent behavior, fate and transport, solvent site cleanup, and decision-making are given below.

1. Pankow, J.F. and J.A. Cherry, 1996. Dense Chlorinated Solvents & Other DNAPLs in Groundwater, Waterloo Educational Services Inc., Rockwood, Ontario.
<http://www.amazon.com/gp/product/0964801418/103-1522514-8943817?v=glance&n=283155>
2. Cohen, R.M., and J.W. Mercer, 1993. DNAPL Site Evaluation. CRC Press, Boca Raton, FL.
3. The Strategic Environmental Research and Development Program (SERDP) and the related Environmental Security Technology Certification Program (ESTCP) are currently funding a number of projects in the area of chlorinated solvent source zone characterization and remediation. The most recent annual report is at
<http://www.serdp.org/research/CU/DNAPL%20ANNUAL%20REPORT-2004.pdf>.
4. The ESTCP program convened a workshop to address the research needs in this area. The workshop report is at
<http://www.estcp.org/documents/techdocs/chlorsolvcleanup.pdf>.
5. Further information on SERDP- and ESTCP-funded research in this area is available at
<http://www.serdp-estcp.org/DNAPL.cfm>.
6. The USEPA sponsored an Expert Panel to assess the benefits of source zone remediation. Their report, DNAPL Remediation: Is There a Case for Source Depletion? is at
<http://www.epa.gov/ada/download/reports/600R03143/600R03143.pdf>
7. The USEPA also recently published a document, Appropriate Goals for DNAPL Source Zone Remediation, available at http://gwtf.cluin.org/docs/options/dnapl_goals_paper.pdf.
8. The National Research Council recently published a review of the field: NRC, 2004. Contaminants in the Subsurface: Source Zone Assessment and Remediation, at
<http://www.nap.edu/openbook/030909447X/html/332.html>.
9. The Interstate Technology and Regulatory Consortium published several documents on DNAPLs, including:
 - An overview of characterization and remediation technologies:
<http://www.itrcweb.org/Documents/DNAPLs-1.pdf>
 - A regulatory review of the challenges of source zone remediation:
<http://www.itrcweb.org/Documents/DNAPLs-2.pdf>
 - An overview of bioremediation of DNAPLs:
<http://www.itrcweb.org/Documents/BioDNAPL-1.pdf>.
10. The Air Force Center for Engineering and the Environment (AFCEE) has a web page with a number of documents, software, and other tools for chlorinated solvents and other contaminants, at <http://www.afcee.brooks.af.mil/products/techtrans/>.

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