

DECISION GUIDE

A Guide for Selecting Remedies for Subsurface Releases of
Chlorinated Solvents

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This ***“Guide for Selecting Remedies for Subsurface Releases of Chlorinated Solvents”*** provides an overview of current knowledge regarding management of subsurface chlorinated solvent releases. The envisioned audience is state regulators, federal regulators, consultants, 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 efforts to clean up subsurface releases, 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 Guide and its companion document, ***“Frequently Asked Questions Regarding Management of Chlorinated Solvents in Soils and Groundwater”***, 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 the 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 COVER and other portions of this document include lithographic prints from John Wesley Powell’s *The Exploration of the Colorado River and Its Canyons* (used with permission from Dover Publications, Inc.). Much like Powell’s 1869 survey of the Colorado River, our effort to resolve issues posed by subsurface releases of chlorinated solvents 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.

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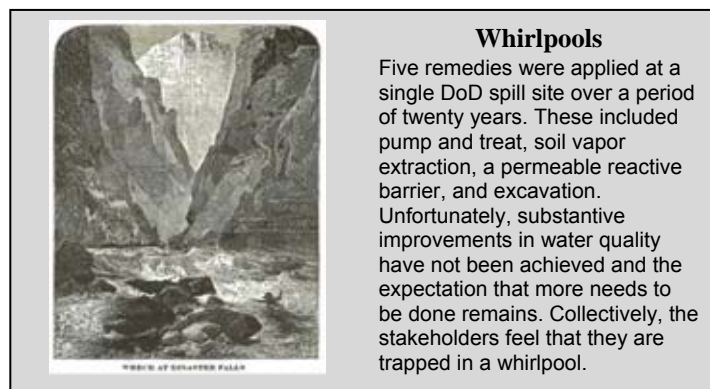
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Section 1 – Introduction

Over the past 30 years we have made enormous progress in managing a legacy of inadvertent releases of chlorinated solvents to subsurface soils and groundwater. First, adverse exposure to chlorinated solvents has been eliminated at almost all sites where chlorinated solvent releases occurred. Second, our understanding of the behavior of chlorinated solvents in subsurface environments has advanced to a state approaching maturity. Last, the cost and performance of a diverse set of remedies is largely understood.

Unfortunately, despite our successes, challenges remain. In particular, far too often employed remedies fail to achieve closure and unanticipated further action is expected. At some DoD facilities this scenario has progressed through multiple iterations. The perceived “whirlpool” creates a sense that we are using available resources inefficiently (NRC 1994, NRC 2005). Considering the finite resources available for cleanup and currently available knowledge, it is clear that we must and can manage chlorinated solvent releases more successfully in the future.

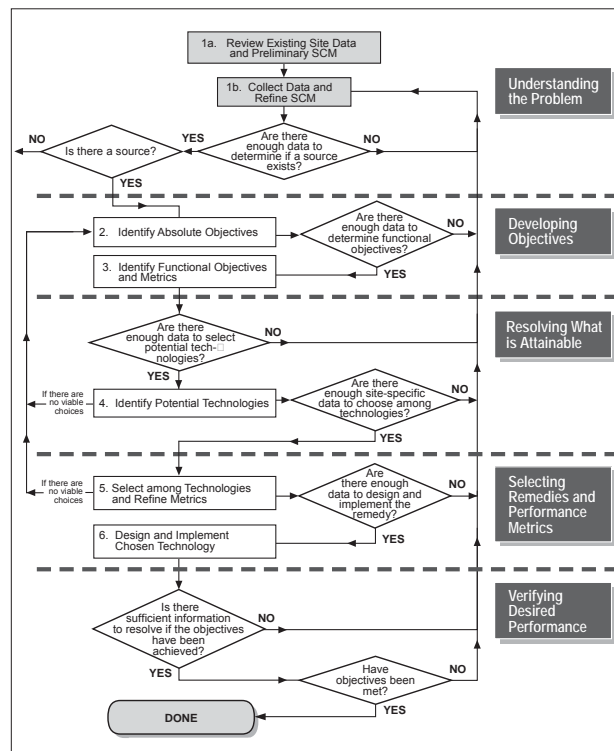


Perceiving an opportunity to “do better,” the Department of Defense’s (DoD) Environmental Security and Technology Certification Program (ESTCP) funded development of this guide to selecting remedies for chlorinated solvent releases and a companion document titled “Frequently Asked Questions About Managing Releases of Chlorinated Solvents to Soils and Groundwater.” The Frequently Asked Questions document serves as an avenue to key concepts for those with limited time. The decision guide (this document) provides more detailed information. The overarching objective of

both documents is to provide easy access to knowledge that supports sound decisions and frequent successes with managing subsurface releases of chlorinated solvent.

This document is targeted at individuals involved in selecting remedies for chlorinated solvents releases. In the case of DoD sites, this typically involves state regulators, federal regulators, consultants, DoD staff, and members of the local community. Addressing this audience reflects the fact that these parties select remedies, access performance, and ultimately hold the responsibility for results.

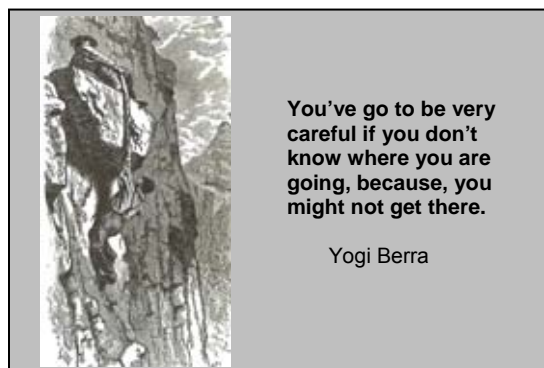
Following the National Research Council's 2005 report - Contaminants in the Subsurface - this document is organized into four sections (see adjacent figure excluding the last element). The first explores the nature of the problem of chlorinated solvents in subsurface environments. Fortunately, through the investments of Strategic Environmental Research and Development Program (SERDP) and ESTCP and others, many of the key pieces of this puzzle have come together in the last few years. First, it is recognized that managing chlorinated



solvents often involves more than managing Dense Non-Aqueous Phase Liquids (DNAPLs). Vapor, dissolved, and sorbed phase chlorinated solvents (particularly those that occur in low permeability zones) often govern what can be achieved with current remediation technologies. This has led to an emerging appreciation of the fact that there are important differences in the ways in which various hydrogeologic settings store and release contaminants, and that these settings control how sites evolve with time and respond to remediation efforts.

The second section addresses developing objectives for sites. An emphasis is that objectives need to be **beneficial**, **attainable**, and **verifiable**. An absence of any one of the attributes diminishes the probability of success. Furthermore, they need to reflect the needs and values of the involved parties. Consideration is given to absolute objectives

that describe broad social goals and functional objectives that serve as a basis for designing solutions. This section also reiterates the National Research Council's prescription for making remediation more successful: greater discipline in developing goals and more evaluation of the probability of success prior to implementing a cleanup project (NRC, 2005).



The third section provides an introduction to what we can expect from proven remediation technologies. This section recognizes that the potential for success of any technology is strongly dependent on the geologic setting and the end state that is trying to be achieved. Emphasis is given to what technologies are likely to remove and what they are likely to leave in place. Knowledge in this section builds on numerous SERDP and ESTCP Reports addressing performance of remediation technologies.

Last, the topic of developing remedial packages for dealing with the challenge of chlorinated solvent releases is addressed. This section recognizes that solutions require not only the selection and implementation of specific technologies, but also a higher-level, holistic view of sites and their challenges. Key factors that need to be considered include subsequent land use, contingencies for variations from anticipated outcomes, addressing the needs of all stakeholders, and maintaining realistic expectations regarding what can be accomplished. Developing remedial packages is often a daunting task. Common challenges include:

- Differences in expectations from involved parties
- The possibility of large uncertainty regarding subsurface conditions
- The fact that the most common requirement for closure (near-term attainment of drinking water standards (maximum concentration levels or MCLs) in groundwater at all points) has rarely, if ever been achieved
- The fact that finite funds are available, considering numerous social priorities.

The challenge of selecting and evaluating remedies is illustrated by a 2004 Navy Survey

(Geosyntec, 2004). The Navy respondents indicated that the remedies were perceived to be a “success” or “fair success” at 55 of 56 evaluated sites. At the same time, the survey authors reported that “none of the remediation attempts presented in this survey/review achieved MCLs or regulatory site closure.” The authors pointed out that achieving MCLs was not always the reason for performing the remediation project, and that “other tangible and intangible criteria ... are used to interpret success.”

The dichotomy between perceived success and the lack of absolute success (restoring groundwater to drinking water conditions) is explained by initial goals such as meeting the planned expenditure, advancing new technology, meeting regulatory expectations, and doing the best that one can. In regards to these objectives, the decision-makers were often successful. On the other hand, endpoints that provide closure and/or dramatically reduce the cost of long-term site care are (in the authors’ experience) rare.

Our philosophy in this decision guide and the companion FAQ document is not to be prescriptive. How decisions are made and the values employed in selecting remedies need to be tailored to the needs of the stakeholders. In addition, a primary theme in this document is pragmatism, reflecting our perspective that the greatest progress can be achieved by focusing on that which is beneficial and attainable.

**"A pragmatist turns towards concreteness
and adequacy, towards facts, towards
action and towards power"**

William James

“The high ground lies in the middle”

R. Allan Freeze, *The Environmental Pendulum*

In summary, the information presented herein is intended to assist decision-makers with selecting remedies for releases of chlorinated solvents to the subsurface environment. Content includes a review of the nature of the problem, consideration of the critical components of setting objectives, a current overview of available options, and suggestions for developing comprehensive remedial packages. Collectively, the goal is to have a high frequency of success with chlorinated solvent sites, with the benefits of a cleaner environment and the opportunity for DoD and others to better focus on their core missions.

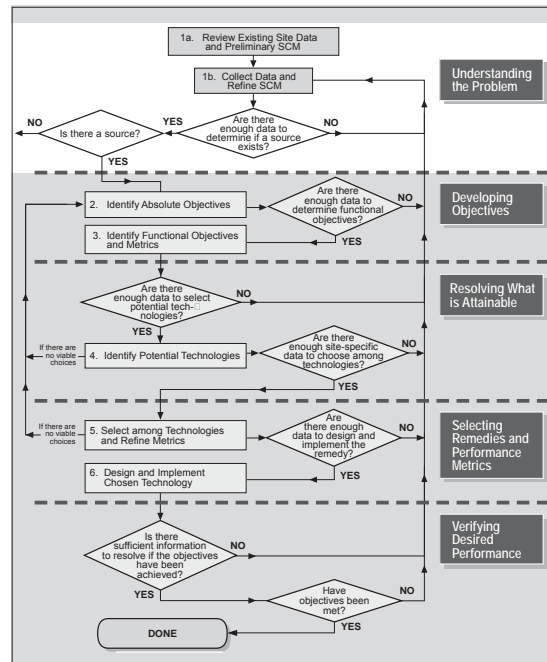
Section 2 - Understanding the Problem¹

The following section describes the behavior of chlorinated solvents in subsurface environments. As shown in the adjacent image (adapted from NRC 2005), having a clear and holistic understanding of the problem is the first step in advancing a sound solution at solvent sites.

To start, this section describes processes governing the *movement* and *distribution* of chlorinated solvents in subsurface environments. It describes the mechanisms of contaminant storage, release, and transport in source and plumes. Furthermore, it provides an introduction to the 14 Compartment Model, a new and powerful graphic decision tool that is a cornerstone of this document.

Next, critical attributes of common geologic settings are identified. Building on work by the National Research

Council (NRC, 2005), five hydrogeologic “type settings” are advanced. Each of these type settings has potentially unique mechanisms for storing chlorinated solvents and responses to remedial actions. Emphasis is given to the fact that the nature of the problem in each setting evolves with time and involves early, middle and late stages.



¹ The following section of this report was written for this document. Subsequently, with permission from ESTCP and Springer Publishing it was edited and published as Chapter 7 In Situ Remediation of Chlorinated Solvent Plumes, Editors H. Ward and H. Stroo, Springer, New York, pp.85-117

Last, the current state of knowledge regarding how source control measures affect contaminant concentrations in downgradient plumes is reviewed. Given that plumes represent a primary exposure pathway, this is a critical concern.

Processes Governing the Movement and Distribution of Chlorinated Solvents in Subsurface Environments

This section presents an overview of processes governing the movement and distribution of chlorinated solvents in source zones and plumes. As a first step, it is critical to recognize that chlorinated solvents in subsurface environments occur in four different phases:

- A *gas* phase in soil vapor
- Dense Nonaqueous Phase Liquid (*DNAPL*)
- A *dissolved* phase in water
- A *sorbed* phase on aquifer solids

Second, it is essential to recognize that each phase can exist in either *transmissive* or *low permeability* geologic media present in source zones and plumes. Distinguishing between transmissive and low permeability zones is extremely important because contaminants in transmissive zones are found in moving groundwater, while contaminated groundwater in a low permeability zone is largely stagnant. Payne et al. (2008) advances this conceptualization by describing aquifers as bodies containing *mobile* and *immobile* pore space. Understanding the mass transfer of chlorinated solvents between transmissive zones (mobile pore space) and low permeability zones (effectively immobile pore space) is essential to understanding the remediation of chlorinated solvent releases.

Building on the four phases, the important distinction between transmissive and low permeability zones, and source and plume, Table 1 delineates 14 compartments in which chlorinated solvents occur. A key attribute of the system of 14 compartments is that it provides a new and holistic view of the problem of chlorinated solvents in subsurface environments that blends hydrogeology, contaminant phases, and location.

Table 1 – 14 subsurface compartments potentially containing chlorinated solvents. Arrows show mass potential transfer links between compartments. Dashed arrows indicate irreversible fluxes.

Phase/Zone	Source Zone		Plume	
	Low Permeability	Transmissive	Transmissive	Low Permeability
Vapor				
DNAPL			NA	NA
Aqueous				
Sorbed				

NA – As per the definition of source zones in NRC (2006), DNAPLs are only present in sources zones and consequently are absent in plumes.

Referred to as “The 14 Compartment Model,” Table 1 is used as a conceptual tool through the remainder of this document. A simple example of the utility of the 14 Compartment Model comes through consideration of a remedy involving extraction of groundwater (pump and treat) from the body in which DNAPL was released (a source zone). The primary effect of pump and treat is to deplete aqueous phase solvents in transmissive zones. A secondary effect is the slow release of solvents stored in other impacted compartments (e.g., DNAPL in transmissive zones and/or dissolved and sorbed chlorinated solvents in low permeability zones). These processes are described in detail in Section 4 of this document. Unfortunately, slow release of solvents from compartments that are not directly addressed can create a need to extract groundwater from source zones for decades or even centuries. The remainder of this section addresses key attributes of chlorinated solvent releases by describing the four phases of concern.

It is important to realize that the 14 Compartment Model is a useful tool, but it is only part of a conceptual site model. Explicitly considering the 14 Compartment Model helps ensure that all of the different phases and transmissive zones are considered when making management decisions. But it is also important that a conceptual site model include a mass balance that addresses the spatial distribution of the mass of contaminants, and the fluxes of contaminants within the site, as well as the hydrogeologic and biogeochemical information needed to evaluate fate and transport. The use of the

14 Compartment Model is designed to encourage the development of integrated strategies, in conjunction with the other aspects of a quantitative conceptual site model.

DNAPL

Subsurface environments consist of solids (e.g., soil, grains, or rock) and void space (soil pores or fracture apertures). The void space contains water above and below the water table. In the unsaturated zone, air coexists with pore water. Compared to air, water is preferentially attracted to solids and forms a continuous “*wetting phase*” that covers the matrix solids and fills the smaller pore spaces. In larger pores, water tends to occupy margins, leaving the remaining central portions filled with air, present as a “*non-wetting phase*.” Figure 1 shows porous media that contains both wetting and non-wetting phases. Recognizing the coexistence of multiple phases (e.g., water, air, and DNAPL), which can be closely commingled in tiny pores, is a key element of understanding mass transfer between phases.

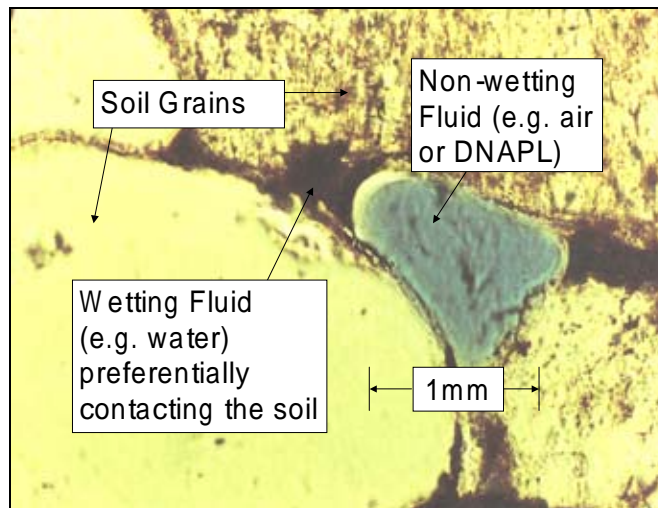


Figure 1 - Immiscible fluids in the pore space of a granular porous media (after Wilson et al., 1990)

Driven by gravity and capillary forces, DNAPL released at the surface migrates downward through the subsurface. Capillary forces reflect the tendency of wetting fluids to be drawn into porous media due to liquid-liquid attraction or liquid-solid attraction (e.g., water being drawn into a dry sponge). Above the capillary fringe, DNAPL displaces air and typically occurs as an intermediate wetting phase between water and air. Over time, volatile DNAPL components partition into soil gas. This produces vapor plumes near

releases. Given a sufficiently large release, DNAPL will migrate into and below the water table. In the groundwater zone, DNAPL displaces water and occurs (typically) as a non-wetting phase. With time, soluble constituents in DNAPL partition into groundwater, forming aqueous plumes in transmissive zones downgradient of the DNAPL zone. An interesting aspect of this process is that the formation of plumes comes with depletion of DNAPL and, ultimately, all of the DNAPL will be depleted.

The occurrence of chlorinated solvents as an immiscible non-wetting phase in the saturated zone influences the movement and ultimate distribution of DNAPL. For DNAPL to invade water-saturated media, it must displace the water. This requires that pressure in the DNAPL be greater than the water pressure by an amount known as the *displacement pressure* (Corey 1994). For a given DNAPL, the displacement pressure is related to the size of the pore. For larger pores the displacement pressure for DNAPL is low, and conversely, for small pores the DNAPL displacement pressure is high.

Given the heterogeneous nature of geologic media and the mechanics of multiphase flow, DNAPL in the saturated zone preferentially invades intervals with the largest pores. Conceptually, this leads to sparse DNAPL bodies described as pools (horizontal subzones) and fingers (interconnecting vertical tubes) that occupy only a small volume of the available pore space. This conceptualization is based on field experiments (e.g., Poulson and Kueper, 1992; Kueper et al., 1993) and theoretical developments (e.g., McWhorter and Kueper, 1996).

Initially, the fraction of pore space filled with DNAPL (pore saturation) is large enough that the DNAPL bodies are continuous (i.e., there are interconnected DNAPL-filled pores). Over time, the DNAPL is depleted through drainage, dissolution, and/or volatilization. These processes reduce DNAPL saturations and transform the continuous DNAPL flow paths into discontinuous ganglia and blobs (Wilson et al., 1990). DNAPL ganglia and blobs are largely immobile as separate phase liquids. Eventually, all of the DNAPL will be transferred to dissolved, vapor, and sorbed phases. Given all of this, the nature of the problems associated with chlorinated solvent releases changes with time.

The architecture of DNAPL pools and fingers within the subsurface is dependent on numerous factors including geology, the rate at which the DNAPL was released, the volume of the release, and the age of the release (Feenstra et al., 1996). Figure 2 (from Feenstra et al., 1996) illustrates four conceptual DNAPL architectures in alluvium, containing both granular and fractured media. The presence of a low permeability layer plays a primary role in defining where the pools occur. DNAPL tends to perch above any

low permeability capillary barrier. In general, rapid releases are thought to create more horizontal spreading while slower releases create less horizontal spreading (Feenstra et al., 1996). Last, DNAPL in fingers is likely to be depleted far more quickly than DNAPL in pools because the geometry and orientation to groundwater flow of DNAPL in ganglia creates a relatively large surface area exposed to flushing (Sale and McWhorter, 2001). Therefore, DNAPL in fingers may be present only during the early stages of a release.

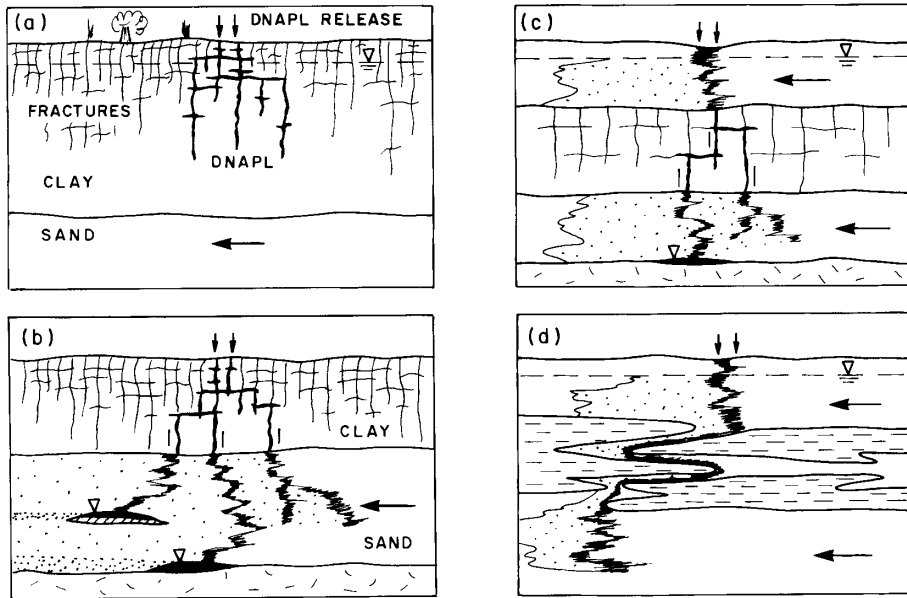


Figure 2 – Examples of DNAPL architecture (Feenstra et al., 1996).

In more detail, Figure 2 Panel “a” represents DNAPL in a fractured clay system, where DNAPL is present in a network of natural fractures in the clay. Panel “b” represents the same conditions as panel “a”, but with enough DNAPL released to penetrate into underlying clay, forming fingers and pools. Panel “c” shows a complex site, where a sand unit with DNAPL is underlain by what would be considered an aquitard, but in this case is fractured to the extent that DNAPL penetrates into the next deepest sand layer. Panel “d” shows complex vertical and lateral movement of DNAPL due to unfractured low-permeability zones. The distribution of DNAPL is controlled by the hydrogeology and the release characteristics of each example site.

Critically absent in Figure 2 are rigorous representations of vapor plumes, groundwater plumes, and solvents sorbed onto aquifer solids. Note that DNAPL is just one of the four phases that can sustain contamination in groundwater and vapor plumes, and more importantly, the distribution between the four phases will change over time as the source ages.

Per Cohen and Mercer (1993), the total mass of solvents in a volume of porous media is the sum of the nonaqueous, aqueous, vapor, and sorbed phases. At any point in space each of the phases is trying to equilibrate with the other phases.

$$\omega_{Total} = \omega_{DNAPL} + \omega_{aqueous} + \omega_{vapor} + \omega_{sorbed}$$

where ω is the mass of contaminant (e.g., chlorinated solvent) per unit mass porous media.

Vapor Phase

Vapor phase chlorinated solvents originate from direct volatilization of DNAPL in the unsaturated zone or from volatilization of aqueous phase chlorinated solvents in pore water to air in the subsurface. Critically, chlorinated solvents are also present as a sorbed phase on solids. Given close commingling of fluids (millimeter or less) chlorinated solvents readily partition between each of the phases.

Under natural conditions, the primary transport process for vapor phase chlorinated solvents is *gas phase diffusion*. This reflects the volatility of chlorinated solvents and large gas phase diffusion coefficients (potentially four orders of magnitude greater than aqueous phase diffusion coefficients). At any point in a porous media, the effective diffusion coefficient is strongly dependent on water content. As water content increases, the cross-sectional area available for vapor phase transport decreases and the tortuosity of the flow paths increase. Higher water content leads to a reduced effective diffusion coefficient.

Transport of vapor phase chlorinated solvents also occurs via *advection* of the vapor phase. Advection can be driven by volatilization of DNAPL, changes in atmospheric pressure, engineered systems (e.g., soil vapor extraction) and negative pressure in buildings.

As chlorinated solvent vapor plumes expand, contaminants partition into pore water and adsorb onto the matrix solids. Initially, this process retards the expansion of vapor

plumes. At later times, chlorinated solvents stored in pore water and sorbed to solids can sustain vapor plumes. Degradation of parent chlorinated solvents in unsaturated zones via biologically mediated processes may not be an important consideration at most sites due to presumed aerobic conditions in most unsaturated zones away from source zones (although recent research indicates limited degradation may be occurring at many sites). Important exceptions are degradation products such as vinyl chloride, dichloroethene, and methylene chloride, which readily degrade under aerobic conditions in vapor plumes.

Vapor plumes present two primary challenges. First, they can contaminate underlying groundwater via diffusion and/or percolation of soil water through the unsaturated zone. Second, vapor plumes can adversely impact indoor air quality. Both of these conditions are common drivers for remedial actions.

Aqueous Phase

As soon as DNAPL encounters water in the subsurface, constituents in the DNAPL begin to partition into water they share pore space with. In both saturated and unsaturated zones, mass transfer occurs between phases in small pore spaces where solids, water and DNAPL are closely commingled. Dissolution of DNAPL constituents into water is driven by differences in the constituents' chemical potential between the DNAPL phase and water phase (Schwarzenbach et al., 1993). Once the chemical potentials in the separate phases equilibrate, the constituents in the aqueous phase reach their effective solubility. Effective solubility is primarily a function of the compound's pure phase solubility and its mole fraction in the DNAPL (Feenstra et al., 1996).

Over time, advection, dispersion, diffusion, and degradation drive dissolved constituents away from DNAPL zones. This depletes aqueous phase chlorinated solvents at the water-DNAPL interfaces and allows for further dissolution of DNAPL. Ultimately, the rate of DNAPL dissolution is governed either by the local rate at which constituents can partition into groundwater (Miller et al., 1990; Powers et al., 1991), or by the rate at which dissolved phase constituents migrate away from the DNAPL (Sale and McWhorter, 2001).

Within transmissive portions of the saturated zone, advective transport produces groundwater plumes that can extend over large distances, for as much as several miles in some cases. As plumes advance, dissolved phase solvents are lost through sorption, diffusion into low permeability layers, and degradation. At some sites, natural rates of

attenuation are rapid enough to create stable or even shrinking plumes (Wiedemeier et al., 1999), and risks to receptors can be addressed through natural processes. Unfortunately, natural attenuation alone is often insufficient to address potential adverse impacts of chlorinated solvent releases.

Dissolved phase constituents also migrate into low permeability zones such as clay lenses and aquitards. Note that with the exception of secondary permeability features (e.g., fractures, root holes, animal burrows), high displacement pressures typically preclude DNAPL from low permeability layers. Dissolved phase constituents, however, can permeate low permeability zones through a combination of diffusion and slow advection. Within low permeability zones, chlorinated solvents are present in both dissolved and sorbed phases. Often, fine-grained low permeability zones have higher sorption capacities due to their greater organic carbon contents and higher surface area per unit volume than adjacent transmissive zones comprised of sands and/or gravels. Higher organic carbon content increases the contaminant storage capacity of low permeability layers and accelerates the diffusion of chlorinated solvents into the low permeability materials (e.g., Parker et al, 1994 and Sale et al, 2008).

As long as the concentration of aqueous phase solvents is greater in the transmissive zones than in the low permeability zone, solvents will be driven into the low permeability zones. This *matrix storage* can be an important mechanism for attenuation of solvents in plumes. However, once the aqueous concentration of the solvents declines in the transmissive layer(s), solvents will begin diffusing back out of the low permeability layers. This process, back diffusion, can sustain plumes for long periods of time (e.g., Liu and Ball, 2002; Chapman and Parker, 2005; AFCEE, 2007; and Sale et al. 2008). Because back diffusion is far slower than the initial inward diffusion process (Parker et al. 1996), it can sustain plumes for extended periods even after all DNAPL is depleted (Figure 3).

Degradation of Chlorinated Solvents

For many years the prevailing opinion was that aqueous phase chlorinated solvents did not degrade under natural conditions in aquifers. However, in the 1980s several researchers (e.g., Vogel and McCarty, 1985; Wilson and Wilson, 1985) demonstrated that biotic processes could degrade chlorinated solvents under reducing (i.e., anaerobic) conditions. This discovery was largely responsible for the acceptance of natural attenuation as a plume management strategy in the late 1990s (Wiedemeier et al., 1998; 1999).

In addition, research conducted in the 1990s indicated that chlorinated solvents can be degraded abiotically via chemical oxidation (Farquar et al., 1991) and chemical reduction (Gillham and O'Hannesin, 1994). More recently it has been recognized that naturally occurring minerals (e.g., magnetite) can also drive abiotic reduction of chlorinated solvents (Danielsen and Hayes, 2004).

The table below identifies the average carbon oxidation state in common chlorinated solvents and associated degradation products. In general, chlorinated solvents with large oxidation states (CT>PCE, CF>TCE) are prone to degradation via reduction. Conversely, chlorinated solvents with lower oxidation states (CM<DCA, VC<DCE, TCA, MC) are prone to degradation via oxidation.

Carbon Oxidation States			
	Ethenes	Ethanes	Methanes
4			CT
3		PCA	
2	PCE		CF
1	TCE	TCA	
0	DCE		MC
-1	Vinyl Chloride VC	DCA	
-2	Ethene		Chloromethane CM
-3		Ethane	
-4			Methane

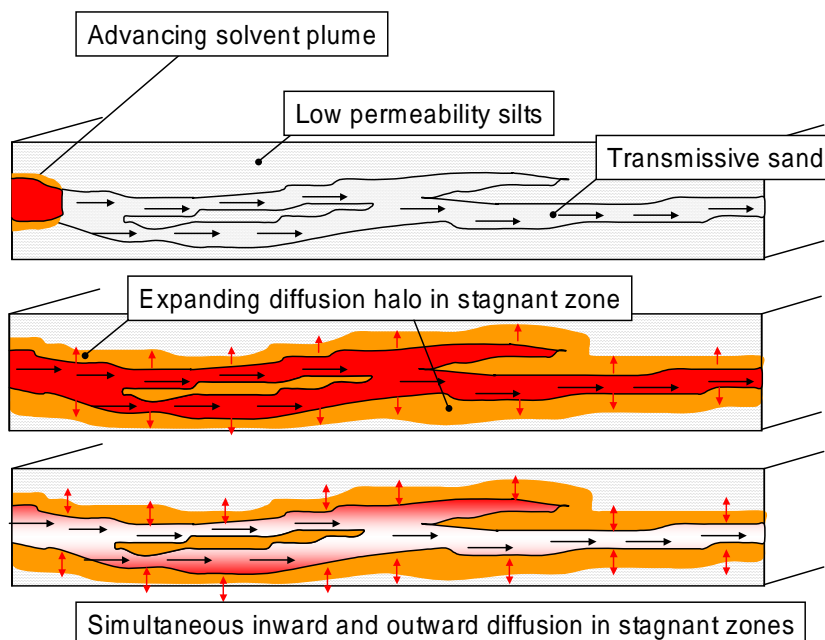
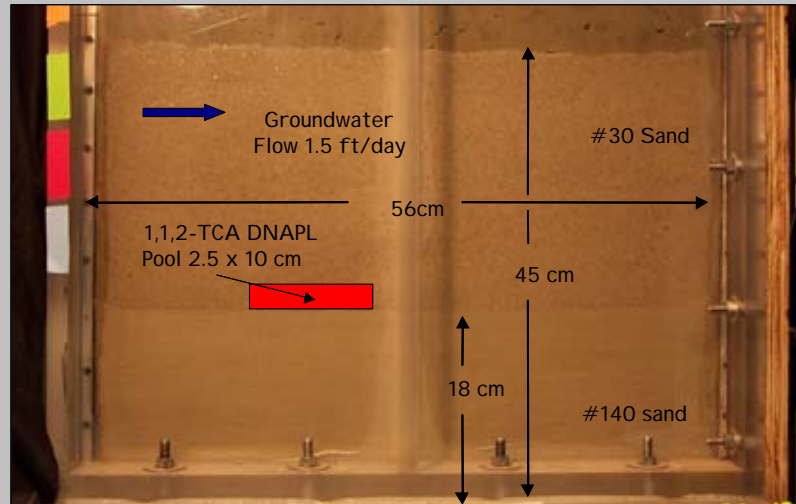


Figure 3 - Diffusion into and out of low permeability materials, leading to initial plume attenuation and subsequent long-term plume persistence (After AFCEE, 2007).

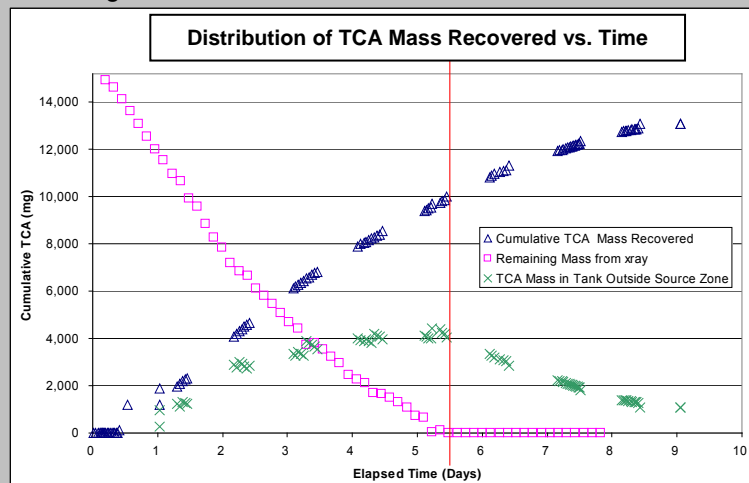
Matrix diffusion and back diffusion have received broad attention. Foster (1975), Tang et al. (1981), Sudicky et al. (1993), and Parker et al. (1996) address diffusion within granular fractured porous media. Freeze and Cherry (1979), Rao et al. (1980), Sudicky (1983), Sudicky et al. (1985), Goltz and Roberts (1987), Wilson (1997), Liu and Ball (2002), Chapman and Parker (2005), AFCEE (2007) and Sale et al. (2008) address diffusion in heterogeneous unfractured granular porous media. The most recent of these publications (Wilson, 1997; Liu and Ball, 2002; Parker and Chapman, 2005; AFCEE, 2007 and Sale et al., 2008), specifically recognize that these processes can impact our ability to restore groundwater quality in source zones and in plumes.

Source strength before and after complete DNAPL dissolution

The following experiment illustrates the dissolution of DNAPL into aqueous phases in a two-layer system (Wilkins, 2005 and AFCEE, 2007). Two layers with an approximate 2 order of magnitude contrast in permeability are present in the sand tank. Water is flushed through the upper transmissive sand layer at a seepage velocity of 1.5 ft/day. A 15-gram pool of 1,1,2-TCA is introduced in the transmissive sand immediately above the low permeability layer.

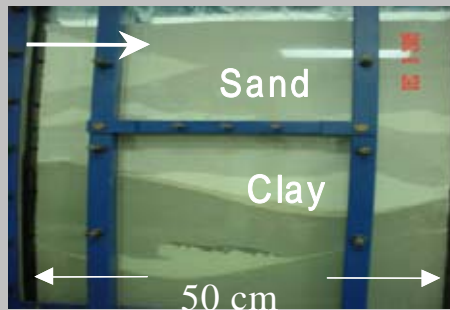


Key results are presented below. The boxes in the graph reflect the amount of DNAPL remaining in the tank as a function of time. This was determined by measuring absorbance of a scanning x-ray source. Results show that the DNAPL completely dissolves in 5.5 days. The triangles depict cumulative aqueous phase discharge of 1,1,2-TCA from the tank. This is based on effluent concentrations and the flow rate through the tank. By the time the DNAPL is fully dissolved, 10 grams of TCA have been discharged from the tank via the transmissive layer. The majority of the remaining 5 grams has been driven into the low permeability layer via transverse diffusion (data posted as X's). Sustained discharge of aqueous phase TCA from the tank after DNAPL depletion (triangles) reflects back diffusion of aqueous phase TCA from the low permeability layer. An interesting observation is that the overall rates of contaminant discharge from the tank are similar with and without DNAPL.

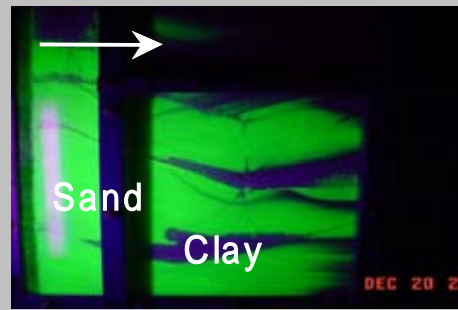


Experiment Illustrating Contaminant Storage and Release from Low Permeability Layers

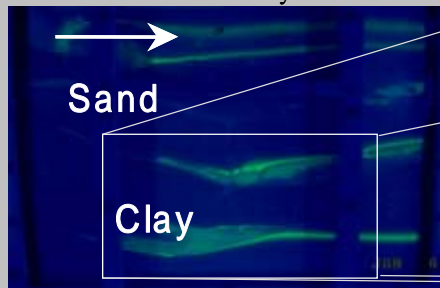
The images below show studies in which water containing fluorescein dye was flushed through a tank containing sand and clay layers (Doner, 2007). Initially the fluorescein is attenuated via diffusion into the clay layers (Panel B). Continued flushing without the fluorescein illustrates how back diffusion from the low permeability clay can sustain contaminant levels in a plume occurring in a transmissive zone in the absence of an upgradient source (Panels C and D).



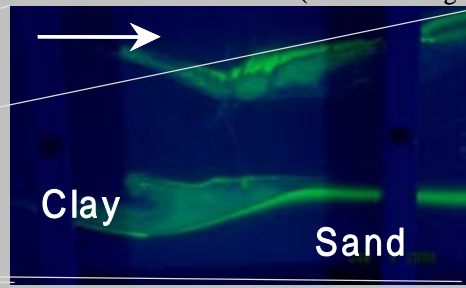
Panel A - Sand and Clay



Panel B - Fluorescein Inflow (Matrix Storage)



Panel C - Source Off – Back Diffusion



Panel D- Close-up of Back Diffusion

Sorbed Phase

The sorbed phase is the contaminant mass that resides in or on the matrix solids. This fraction of the total mass includes both contaminant adsorption onto solid surfaces and absorption of contaminants into the matrix particles. As the aqueous phase concentrations increase, there is a net transfer of contaminants to the sorbed phase. This equilibrium partitioning attenuates and slows the migration of dissolved phase contaminant concentration as the plumes advance by removing dissolved contaminants from the transmissive zone. In addition, it creates an *in situ* reservoir of immobile stored contaminants. The initial process of attenuating aqueous phase contamination via sorption is referred to as retardation.

Conversely, as aqueous phase concentrations decrease as the site ages (due to natural weakening of the source or active source remediation), contaminants are released from the sorbed phase back into the aqueous phase. This desorption has the net effect of sustaining the aqueous phase concentrations. As a first order approximation, the amount of sorbed contamination is proportional to the fraction of organic carbon (f_{oc}) present in the porous media and the compound's organic carbon partitioning coefficient (K_{oc}). Greater detail is provided in Karickhoff et al. (1979) and Schwarzenbach et al. (1993).

To illustrate the relative distribution of the aqueous and sorbed phase contaminant mass, Figure 4 plots the contaminant fraction present in the aqueous and sorbed phases, given a typical range of f_{oc} values. At a high organic carbon content ($f_{oc} > 0.01$), more than 90 percent of the contaminant mass is present as a sorbed phase. Given high surface areas and deposition in quiescent environments, this is a plausible scenario for silts or clay deposited in an organically rich environment. At the low end of the range of organic carbon contents ($f_{oc} < 0.001$), only 10 to 20 percent of the total contaminant mass may be stored in the sorbed phase.

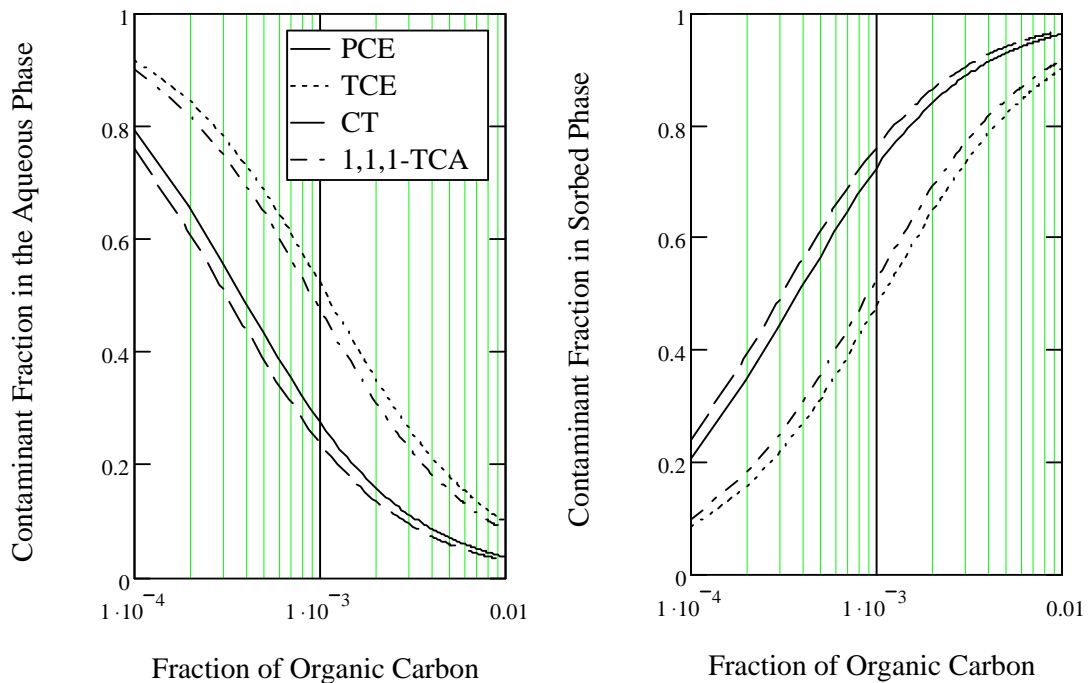


Figure 4 – Fractions of total contaminant mass in the aqueous and sorbed phases as a function of the fraction of organic carbon (Following Schwarzenbach et al. (1993), using parameters for typical saturated soils and K_{oc} values from Allen-King et al. (1996)).

More recently, several researchers have determined that sorption and desorption have a linear relationship only at higher concentrations, and at lower concentrations a hysteretic effect is observed due to availability effects (e.g., Pignatello and Xing, 1996). Some researchers call this hysteresis effect “dual-equilibrium desorption” (Chen et al., 2004). Like matrix diffusion, desorption can sustain low-concentration groundwater plumes for long periods of time.

Critical Attributes of Common Geologic Settings

As stated in NRC (2005), “Subsurface settings are a product of a set of diverse geologic processes that produce an abundance of variation.” These “geologic variations” play a primary role in controlling the distribution of chlorinated solvents in subsurface environments, and are critical to understanding of how chlorinated solvent releases evolve with time. Geologic variations also control the effectiveness of remedial actions. The following a) introduces five geologic “type settings” and b) contemplates how solvent releases in each type setting will evolve with time.

Geologic Type Settings

NRC (2005) describes five general geologic type settings (Figure 5). In the interest of consistency, the portions of the following text in italics are direct quotes from NRC (2005).

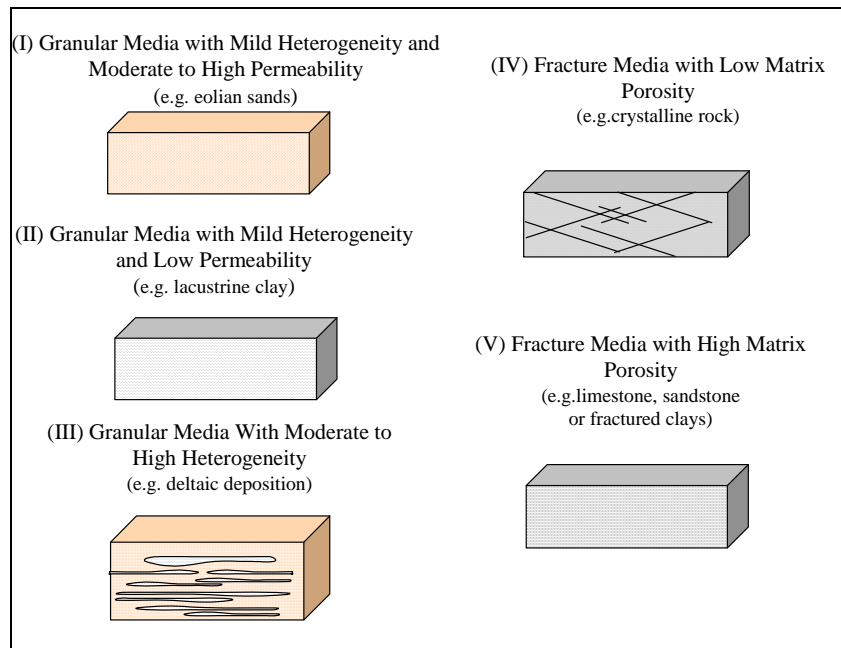


Figure 5 – Geologic Type Settings (NRC 2005)

Type I – Granular Media with Mild Heterogeneity and Moderate to High Permeability

Type I media include systems with porosities that are consistent with typical granular media (e.g., 5 percent to 40 percent), permeability values that are consistent with sand or gravel deposits ($>10^{-14}$ m² or hydraulic conductivity $>10^{-7}$ m/s), and mild heterogeneity (less than three orders of magnitude). As conceptualized, this material is about as uniform as it can be in nature and thus is relatively uncommon. Deposits of this nature are encountered in association with windblown sands and beach deposits. Examples include beach sands at the Canadian Forces Base Borden, Canada, and dune deposits at Great Sand Dunes National Park, Colorado (Figure 6).



Figure 6 - Examples of Type I media (Great Sand Dunes National Park web site)

Due to mild heterogeneity and moderate to high permeability, stagnant zones are not dominant in Type I settings and there is little contaminant storage in low permeability layers (sorbed or dissolved). The dominant storage/release mechanism will be associated with DNAPL dissolution and solid-phase sorption.

Type I settings are relatively rare. On the other hand, they have been widely represented in laboratory experiments using columns or tanks (e.g., Schwille, 1988). As such, they provide a viewpoint for our conceptualization of chlorinated solvents in subsurface environments. However, the predominance of research studies conducted in Type 1 settings have led to an underappreciation of the importance of heterogeneity in other geologic settings.

Type II – Granular Media with Low Heterogeneity and Low Permeability

Type II settings have porosities that are consistent with typical granular media (e.g., 5 percent to 40 percent), low spatial variation in permeability (less than three orders of magnitude), low permeability consistent with silt or clay deposits ($k < 10^{-14}$ m²), and low hydraulic conductivity ($K < 10^{-7}$ m/s). An example is a clay deposit with no significant secondary permeability features (such as fractures, root holes, animal burrows). These systems are uncommon (especially in the near-surface environment where releases typically occur), although some examples include TCE-contaminated clays at the Department of Energy's Savannah River Site in South Carolina. More typically, low-permeability materials contain significant secondary permeability features and thus fit better into the Type V setting description (see below).

In Type II settings the entire zone can be viewed as hydraulically stagnant. The primary contaminant transport process is diffusion. Settings of this nature are difficult to contaminate, and as such, they are not a common concern for remediation efforts.

Type III – Granular Media with Moderate to High Heterogeneity

Type III settings encompass systems with moderate to large variations in permeability (greater than three orders of magnitude) and porosities that are consistent with granular media (e.g., 5 percent to 40 percent). Given large spatial variations in permeability (at the scale of centimeters to meters), portions of the zone are comparatively transmissive while others contain mostly stagnant fluids. As an example, an interbedded sandstone and shale is shown in Figure 7. For the purpose of this report, the more transmissive zones in Type III media have a permeability greater than 10^{-14} m² ($K > 10^{-7}$ m/s). Near-surface deposits of this nature are common due to the abundance of alluvium with large spatial variations in permeability and are encountered in either rock or alluvium associated with deltaic, fluvial, alluvial fan, and glacial deposits. Examples include the Garber-Wellington Aquifer in central Oklahoma, the Chicot Aquifer in Texas and Louisiana, and varved sediments near Searchmont, Ontario.



Figure 7 - Interbedded sandstone and shale, an example of Type III media.
Photo provided by Fred Payne – ARCADIS.

In Type III settings, heterogeneity introduces stagnant groundwater zones to the system. These zones initially attenuate DNAPL constituents that partition into groundwater. After the DNAPL is depleted, the stagnant zones sustain groundwater plumes in transmissive zones. The depositional environments that create low permeability zones often favor higher concentrations of organic carbon. As a result, low permeability layers may have large sorptive capacities, increasing the potential for diffusion into these materials, and enhancing their ability to sustain dissolved chemical plumes after the original chemical source (DNAPL) has been depleted, contained, or remediated.

Type IV - Fractured Media with Low Matrix Porosity

Fractured media with low matrix porosity are common in crystalline rock including granite, gneiss, and schist. Examples include bedrock in the Piedmont and Blue Ridge Mountain region of the southeastern United States and plutonic cores of mountain ranges in the western United States (see Figure 8 for an example). The primary transmissive feature in Type IV settings is the secondary permeability caused by fractures, because little to no void space exists in the unfractured matrix. The permeability of the unfractured matrix is considered to be less than 10^{-17} m^2 ($K < 10^{-10} \text{ m/s}$). However, the bulk permeability of the media is dependent on the frequency, aperture size, and degree of interconnection of the fractures, such that the anticipated range of bulk permeability values is 10^{-15} – 10^{-11} m^2 ($K = 10^{-8}$ – 10^{-4} m/s). The porosity of both the matrix and the fractures is typically small—less than 1 percent. However, in regions where crystalline

rock has been extensively weathered (e.g., at the top of bedrock), the bulk media can behave more like a porous medium than what would be expected from a fractured rock type setting.

In Type IV settings, contaminant transport is primarily limited to fractures and there is little mass storage in low permeability zones, due to low matrix porosity. The primary source is likely DNAPL. Over time, DNAPL will be depleted from the more transmissive fractures and DNAPL in low flow areas (e.g., dead end fractures) will dominate. Due to the combined effects of low matrix attenuation and low fracture porosity, the contaminant migration velocity at a fractured media site can be very rapid and, consequently, these sites can have long plumes (Sudicky et al. 1993; Parker et al., 1996).

A primary challenge in this setting is the complexity of the fractures. The fracture frequencies and their capacity to transmit fluid can be highly variable. Furthermore, the degree to which sets of fractures are interconnected can also be highly variable.



Figure 8 - Fractured crystalline rock, an example of Type IV media (Cache La Poudre River, Colorado, Photo provided by Tom Sale) .

Type V – Fractured Media with High Matrix Porosity

This setting includes systems where fractures (secondary permeability) are the primary transmissive feature and there is large void space in the matrix. The permeability of the unfractured matrix is considered to be less than 10^{-17} m^2 ($K < 10^{-10} \text{ m/s}$). The anticipated range of bulk permeability values is 10^{-16} – 10^{-13} m^2 ($K = 10^{-9}$ – 10^{-6} m/s). The porosity of the fractures relative to the total unit volume is small (e.g., <1 percent). However, unlike Type IV, in Type V hydrogeologic settings the porosity of the unfractured matrix is anticipated to fall in the range of 1 to 40 percent. Fractured media with high matrix porosity are commonly encountered in sedimentary rock (e.g., limestone, dolomite, shale, and sandstone) and fractured clays. Examples include the Niagara Escarpment in the vicinity of the Great Lakes (see Figure 2-7) and fractured lake-deposited (lacustrine) clays in Sarnia, Ontario, Canada.



Figure 9 - Bedding planes, joints, and vertical fractures in carbonate rock, Ontario, Canada (Photo Courtesy of Dr. Beth Parker University of Guelph).

Type V settings introduce stagnant zones to the system. These zones initially attenuate DNAPL constituents that partition into groundwater by diffusion from the fracture zones into the rock matrix. After the DNAPL is depleted, back diffusion sustains dissolved phase concentrations in groundwater flowing in the fractures. For systems where the matrix material has large sorptive capacities, the stagnant zones will act as a contaminant sink and accelerate the rates of natural DNAPL depletion. Due to limited mass storage in fractures, rapid depletion of DNAPL may occur via natural processes (e.g., Parker et al. 1994).

An important variant of the Type V setting is karst, which is common in carbonates (e.g., limestone or dolomite). In this scenario, transmissive zones include sinkholes, caves, and other solution openings that vary widely in aperture and have the potential to store and transport significant contaminant mass (see Figure 10). Permeability in karst terrains varies over tens of orders of magnitude from low permeabilities between fractures to open channel flow in channels and caves (Teutsch and Sauter, 1991; White, 1998; White, 2002). Karst is characterized by both rapid transport along sparse dissolution features and a high ratio of stagnant to transmissive zones. As such, it is one of the most challenging hydrogeologic settings to characterize and manage.

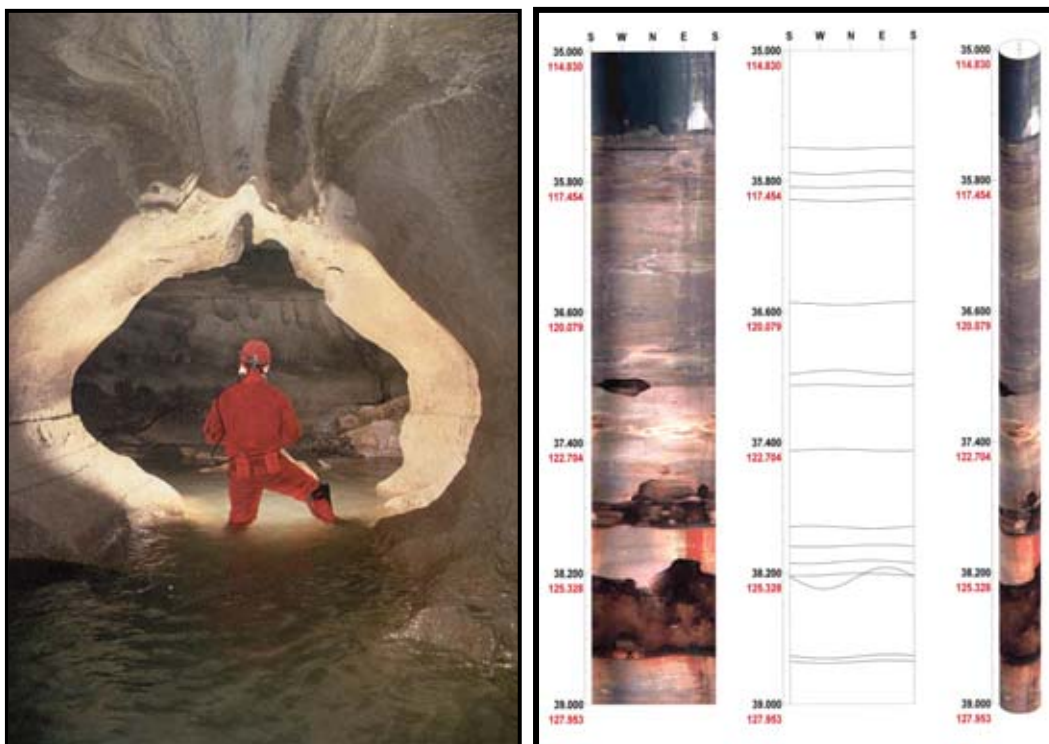


Figure 10 - Large- and small-scale solution features in karst limestone, Redstone Arsenal (Courtesy of Tom Zondlo, Shaw Engineering).

Source Zones Containing Multiple Type Settings

Source zones, especially those above a certain size, may encompass more than one hydrogeologic setting. This commonly occurs in the instance of shallow alluvium over bedrock. For example, in the Piedmont region of the southeastern United States, one can find fluvial deposits (Type III) and saprolite (Type V) overlying fractured crystalline rock (Type IV). Selecting characterization tools and source management technologies is challenging under these conditions, because although contamination may exist

throughout, the appropriate tools for one hydrogeologic setting may not work in the adjacent hydrogeologic setting.

Summary of Type Settings

Table 2 - provides a summary of the geologic type settings described in the prior text.

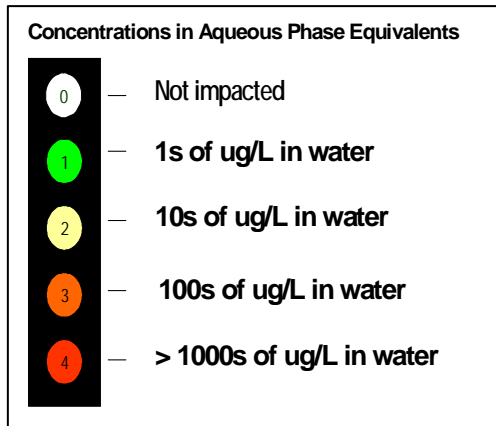
Table 2 – Summary of Geologic Type Settings

Geologic Setting	Permeability (m²)	Hydraulic Conductivity (m/s)	Porosity (%)	Properties
Type I - Granular Media with Mild Heterogeneity and Moderate to High Permeability	$k > 10^{-14}$	$K > 10^{-7}$	5 – 40	<ul style="list-style-type: none"> - Uniform material - Relatively uncommon (e.g., sand or gravel deposits)
Type II - Granular Media with Low Heterogeneity and Low Permeability	$k < 10^{-14}$	$K < 10^{-7}$	5 - 40	<ul style="list-style-type: none"> - Low permeability materials with no secondary permeability features, i.e., fractures (e.g., clay deposit)
Type III - Granular Media with Moderate to High Heterogeneity	$k > 10^{-14}$	$K > 10^{-7}$	5 - 40	<ul style="list-style-type: none"> - Large spatial variations in permeability (e.g., deltaic, fluvial, and glacial deposits)
Type IV - Fractured Media with Low Matrix Porosity	$k < 10^{-17}$	$K < 10^{-10}$	< 1 (both fractures and matrix)	<ul style="list-style-type: none"> - Little void space exists in unfractured matrix - Transmissive features due to fractures (e.g., crystalline rock)
Type V - Fractured Media with High Matrix Porosity	$k < 10^{-17}$	$K < 10^{-10}$	< 1 (fractures) 1 – 40 (matrix)	<ul style="list-style-type: none"> - Large void spaces exist in unfractured matrix - Transmissive features due to fractures (e.g., limestone, sandstone, and clays with secondary permeability features)

Evolution of Chlorinated Solvent Releases as a Function of Setting and Time

It is critical to recognize that chlorinated solvent sites evolve over time; in other words, the location of the mass changes as the site ages. This occurs both with respect to the spatial location of the vapor and dissolved phase plumes, but more importantly, with respect to the distribution of the contaminant mass in the four phases. This process is conceptualized in Figure 11 for a Type III setting (Granular Media with Moderate to High Heterogeneity) underlain by a Type V setting (Fractured Media with High Matrix Porosity). The adjacent image provides a key for the concentrations in each of the compartments.

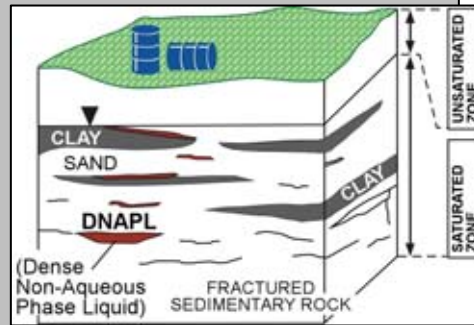
In the initial stage, most of the contaminant mass is found in the DNAPL phase, and this DNAPL is the key problem. During the middle stage, the problem has expanded to all phases in transmissive and low permeability zones in the source and the plume. In the late stages, DNAPL is fully depleted and the problem is dominated by solvents stored in low permeability zones.



Building on the themes in Figure 11, Figure 12 illustrates the evolution of chlorinated solvents in all five type settings. It is important to note that the described distributions are plausible for each type setting but are not necessarily the only possibility. Other distributions in the noted setting at the described stages are possible. For example, vapor plumes may or may not be present depending on the release mechanism and/or the depth to groundwater. The rate at which a DNAPL release matures is dependent on numerous factors including the size of the release, the solubility/volatility of the DNAPL, the hydrogeologic setting, and the local rate of groundwater flow.

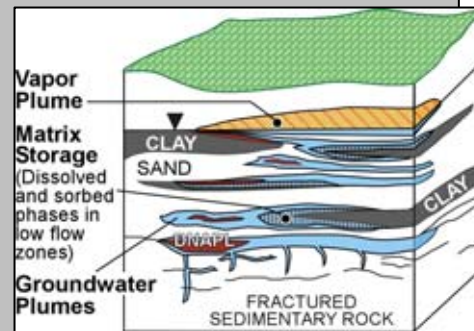
- Early Stage – The majority of the release is present as a DNAPL. Groundwater plumes are just beginning to form and little if any contamination is present in low permeability zones.

Zone/Phases	Source Zone		Plume	
	Low Permeability	Transmissive	Transmissive	Low Permeability
Vapor	0	2	1	0
DNAPL	0	4		
Aqueous	0	2	1	0
Sorbed	0	2	1	0



- Middle Stage – Much of the original DNAPL release (e.g., 50%) has moved into vapor, aqueous, and/or sorbed phases. Large vapor and/or groundwater plumes may be present and contaminants are present in low permeability zones.

Zone/Phases	Source Zone		Plume	
	Low Permeability	Transmissive	Transmissive	Low Permeability
Vapor	2	2	2	2
DNAPL	2	3		
Aqueous	2	3	3	2
Sorbed	2	3	3	2



- Weathered – DNAPL is absent. Plumes in transmissive zones can be sustained by desorption and/or back diffusion from low permeability layers located in the source zone and plume.

Zone/Phases	Source Zone		Plume	
	Low Permeability	Transmissive	Transmissive	Low Permeability
Vapor	3	2	2	3
DNAPL	1	1		
Aqueous	3	2	2	3
Sorbed	3	2	2	3

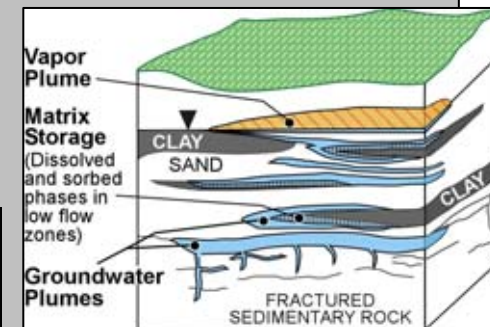


Figure 11 – Evolution of a chlorinated solvent release in a Type III setting as a function of time. Red, yellow, and green compartments indicate high, moderate, and low importance of the compartments, respectively. Noted conditions are plausible, but not necessarily the only possibility.

	Early					Middle					Late									
Type I	Source Zone					Plume					Source Zone					Plume				
	Zone/Phases	Low Permeability	Transmissive	Transmissive	Low Permeability	Zone/Phases	Low Permeability	Transmissive	Transmissive	Low Permeability	Zone/Phases	Low Permeability	Transmissive	Transmissive	Low Permeability	Zone/Phases	Low Permeability	Transmissive	Transmissive	Low Permeability
	Vapor		2	1		Vapor		2	2		Vapor		2	2		Vapor		2	2	
	DNAPL		3			DNAPL		3			DNAPL		0			DNAPL		0		
	Aqueous		2	1		Aqueous		3	3		Aqueous		2	3		Aqueous		2	3	
Sorbed		2	1		Sorbed		3	3		Sorbed		2	3		Sorbed		2	3		
Type II	Source Zone					Plume					Source Zone					Plume				
	Zone/Phases	Low Permeability	Transmissive	Transmissive	Low Permeability	Zone/Phases	Low Permeability	Transmissive	Transmissive	Low Permeability	Zone/Phases	Low Permeability	Transmissive	Transmissive	Low Permeability	Zone/Phases	Low Permeability	Transmissive	Transmissive	Low Permeability
	Vapor	0			0	Vapor	0			0	Vapor	0			0	Vapor	0			0
	DNAPL	0				DNAPL	0				DNAPL	0				DNAPL	0			
	Aqueous	2			0	Aqueous	3			2	Aqueous	3			3	Aqueous	3			3
Sorbed	2			0	Sorbed	3			2	Sorbed	3			3	Sorbed	3			3	
Type III	Source Zone					Plume					Source Zone					Plume				
	Zone/Phases	Low Permeability	Transmissive	Transmissive	Low Permeability	Zone/Phases	Low Permeability	Transmissive	Transmissive	Low Permeability	Zone/Phases	Low Permeability	Transmissive	Transmissive	Low Permeability	Zone/Phases	Low Permeability	Transmissive	Transmissive	Low Permeability
	Vapor	0	2	1	0	Vapor	2	2	2	2	Vapor	3	2	2	3	Vapor	3	2	2	3
	DNAPL	0	4			DNAPL	2	3			DNAPL	1	1			DNAPL	1	1		
	Aqueous	0	2	1	0	Aqueous	2	3	3	2	Aqueous	3	2	2	3	Aqueous	3	2	2	3
Sorbed	0	2	1	0	Sorbed	2	3	3	2	Sorbed	2	3	3	2	Sorbed	3	2	2	3	
Type IV	Source Zone					Plume					Source Zone					Plume				
	Zone/Phases	Low Permeability	Transmissive	Transmissive	Low Permeability	Zone/Phases	Low Permeability	Transmissive	Transmissive	Low Permeability	Zone/Phases	Low Permeability	Transmissive	Transmissive	Low Permeability	Zone/Phases	Low Permeability	Transmissive	Transmissive	Low Permeability
	Vapor		2	1		Vapor		2	2		Vapor		2	2		Vapor		2	2	
	DNAPL		3			DNAPL		3			DNAPL		0			DNAPL		0		
	Aqueous		2	1		Aqueous		3	3		Aqueous		2	3		Aqueous		2	3	
Sorbed		2	1		Sorbed		3	3		Sorbed		2	3		Sorbed		2	3		
Type V	Source Zone					Plume					Source Zone					Plume				
	Zone/Phases	Low Permeability	Transmissive	Transmissive	Low Permeability	Zone/Phases	Low Permeability	Transmissive	Transmissive	Low Permeability	Zone/Phases	Low Permeability	Transmissive	Transmissive	Low Permeability	Zone/Phases	Low Permeability	Transmissive	Transmissive	Low Permeability
	Vapor	0	2	1	0	Vapor	2	2	2	2	Vapor	3	2	2	3	Vapor	3	2	2	3
	DNAPL	0	4			DNAPL	2	3			DNAPL	1	1			DNAPL	1	1		
	Aqueous	0	2	1	0	Aqueous	2	3	3	2	Aqueous	2	3	3	2	Aqueous	3	2	2	3
Sorbed	0	2	1	0	Sorbed	2	3	3	2	Sorbed	2	3	3	2	Sorbed	3	2	2	3	

Figure 12 – Illustration of plausible distributions of chlorinated solvent as a function of type setting and the stage of release. Gray boxes are considered to be absent in the type setting. Red, yellow, and green compartments indicate high, moderate, and low importance of the compartments, respectively. Note that conditions presented are plausible in the noted situations, but not necessarily the only possible scenario.

Figure 12 can be simplified from 15 to 6 scenarios by recognizing that:

- Type Settings I and II are relatively uncommon in natural settings. Even the well-studied Canadian Forces Base Borden site, which is widely viewed as uniform sand, has three orders of magnitude of spatial variation in hydraulic conductivity (Sudicky, 1986) and is underlain by lacustrine clay. Contaminated Type II sites are also relatively rare.
- Overall, early stage sites are very rare. Most of the sites we currently deal with are 30, 40, or even 50 years old.

Given the limited frequency of Type I settings, Type II settings, and early stage conditions,

Figure 13 illustrates the 6 primary scenarios of concern for chlorinated solvent releases.

	Middle					Late																																																														
Type III	<table border="1"> <thead> <tr> <th rowspan="3">Zone/Phases</th> <th colspan="2">Source Zone</th> <th colspan="2">Plume</th> </tr> <tr> <th>Low Permeability</th> <th>Transmissive</th> <th>Transmissive</th> <th>Low Permeability</th> </tr> </thead> <tbody> <tr> <td>Vapor</td> <td>2</td> <td>2</td> <td>2</td> <td>2</td> </tr> <tr> <td>DNAPL</td> <td>2</td> <td>3</td> <td></td> <td></td> </tr> <tr> <td>Aqueous</td> <td>2</td> <td>3</td> <td>3</td> <td>2</td> </tr> <tr> <td>Sorbed</td> <td>2</td> <td>3</td> <td>3</td> <td>2</td> </tr> </tbody> </table>					Zone/Phases	Source Zone		Plume		Low Permeability	Transmissive	Transmissive	Low Permeability	Vapor	2	2	2	2	DNAPL	2	3			Aqueous	2	3	3	2	Sorbed	2	3	3	2	<table border="1"> <thead> <tr> <th rowspan="3">Zone/Phases</th> <th colspan="2">Source Zone</th> <th colspan="2">Plume</th> </tr> <tr> <th>Low Permeability</th> <th>Transmissive</th> <th>Transmissive</th> <th>Low Permeability</th> </tr> </thead> <tbody> <tr> <td>Vapor</td> <td>3</td> <td>2</td> <td>2</td> <td>3</td> </tr> <tr> <td>DNAPL</td> <td>1</td> <td>1</td> <td></td> <td></td> </tr> <tr> <td>Aqueous</td> <td>3</td> <td>2</td> <td>2</td> <td>3</td> </tr> <tr> <td>Sorbed</td> <td>3</td> <td>2</td> <td>2</td> <td>3</td> </tr> </tbody> </table>					Zone/Phases	Source Zone		Plume		Low Permeability	Transmissive	Transmissive	Low Permeability	Vapor	3	2	2	3	DNAPL	1	1			Aqueous	3	2	2	3	Sorbed	3	2	2	3
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Figure 13 – Six primary scenarios of concern for chlorinated solvent releases.

At complex sites it may be difficult to develop a single Fourteen Compartment model that describes conditions throughout an entire release. In these cases it may be useful to divide a release into separate blocks, as shown in Figure 14.

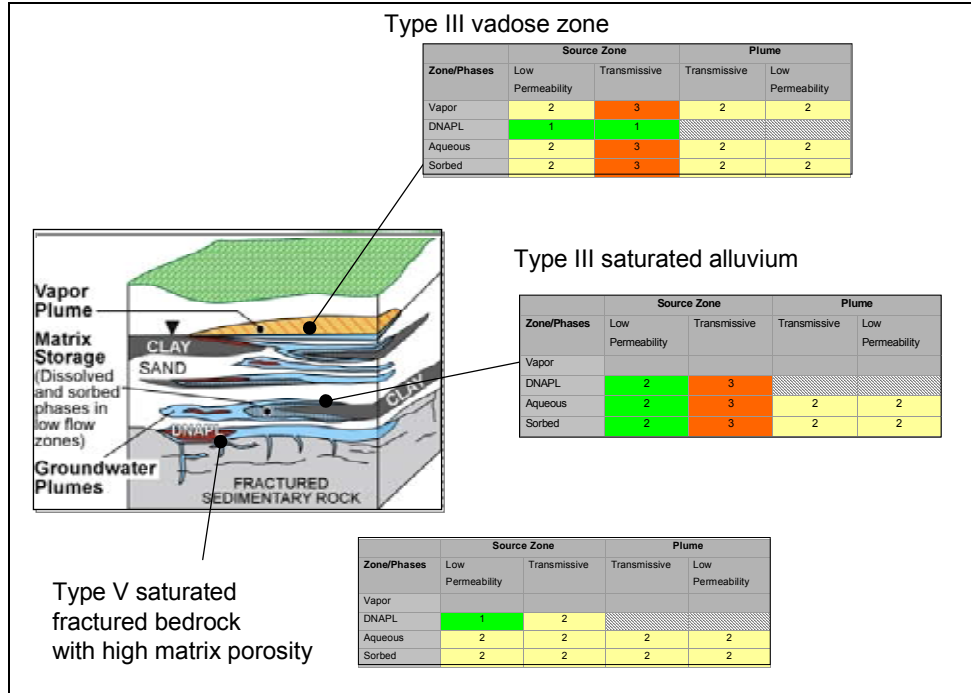


Figure 14 – Use of multiple 14 Compartment Models to describe a complex site.

As noted in the introduction, the 14 Compartment Model drives a holistic view of chlorinated solvents sites which is helpful for making informed decisions. But as was also noted, there are limitations to the model, and a thorough conceptual site model is still required. One potential limitation is that it can be difficult to develop reasonable estimates for all of the compartments. This problem may be common, but it is better to be forewarned than surprised. In the past we have been surprised too many times.

The model often points out the limitations of site characterizations, because in many cases we have characterized sites by relying solely on water quality data from monitoring wells. Groundwater sampling is a useful tool for resolving potential exposures via groundwater, but unfortunately, it typically provides little if any information about vapor, DNAPL, or sorbed phases in transmissive zones and no information regarding contaminants in low permeability zones. Use of the 14 Compartment Model often emphasizes the fact that water quality in wells provides direct insight into only two of the fourteen compartments.

The Effects of Source Depletion or Source Containment on Water Quality

It is fundamental to the process of making decisions regarding source zones to resolve (in advance) how the remedial actions will affect key metrics including (1) contaminant mass discharge from source zones and (2) contaminant concentrations in plumes. For sources, the critical issue is often the magnitude and/or duration of contaminant discharge in units of mass per time (also called contaminant mass flux). For plumes, the critical issue is often the aqueous concentrations in units of mass per volume.

Contaminant discharge from sources can be reduced via containment and/or depletion. Common containment measures include physical barriers, hydraulic capture and/or permeable reactive barriers. Ideal containment measures provide an instantaneous and permanent boundary downgradient of the source, with zero or near zero contaminant flux crossing the boundary. Functionally, containment provides a step function change in contaminant loading to a downgradient plume.

Common source depletion approaches include excavation, soil vapor extraction, *in situ* chemical oxidation, *in situ* chemical reduction (biotic or abiotic) and conductive heating. These measures are likely to provide fractional depletion of the contaminant mass in the source zone and a corresponding fractional reduction in the magnitude and/or duration of the contaminant loading to the plume. What remains in the source after depletion is likely to feed contaminants to the downgradient plume at a rate that decays with time (e.g., Newell and Adamson, 2005; Falta, 2008). Note that the ability to make *a priori* predictions of how source depletion affects contaminant discharge at a field-scale is limited. Challenges include the complexity of field scale sources, the rigor with which subsurface conditions can be resolved (before and after treatment), and the long time periods that are typically required to resolve field-scale responses to source depletion measures.

The second issue—how the contaminant concentrations in the dissolved plumes will respond to upgradient reductions in contaminant loading—can be equally challenging. Reduced loading to plumes can promote desorption of contaminants stored in transmissive zones and/or the back diffusion of contaminants stored in low permeability zones within the plumes. Both processes can sustain plumes for extended periods (Chapman and Parker, 2005; AFCEE, 2007; Sale et al. 2008).

Given uncertainties in our current knowledge of both sources and plume function, opinions about how groundwater plumes respond to interception and/or source depletion

are diverse. Nevertheless, sound decisions for chlorinated solvent sites hinge on understanding how source control measures will affect plumes. With this in mind, the following sections review the current prominent perspectives regarding the effect of source control measures on the contaminant concentrations in plumes.

The Big Picture

Expert panel reports by the U.S. Environmental Protection Agency (USEPA, 2003) and the National Research Council (NRC, 2005) have come to a consensus on two key issues. The good news is that, given effective execution, current source remediation technologies are capable of depleting a large portion of the chlorinated solvents present in the subsurface, and thereby significantly reducing the total loading of chlorinated solvents to plumes. The bad news is that, in most instances, enough contaminated mass will remain after treatment (in source zones and/or plumes) to exceed typical regulatory criteria (maximum contaminant levels [MCLs]) in groundwater for extended periods.

Managers who must make decisions regarding source treatment are therefore confronted with the following:

- On the one hand, source treatment will reduce the ultimate total mass of contaminants in downgradient plumes, and will likely result in reduced plume extent and/or longevity. Although there will probably still be contaminants remaining in the source and plume even after source treatment, the benefits may be significant from an economic or regulatory point of view.
- On the other hand, no matter what type of treatment is done, there may be an ongoing expectation that remaining contaminant will be addressed through further investments in source depletion and/or plume management. These ongoing site care requirements can lead to questions about the value of any source treatment, especially since the cost of source treatment can be substantial.

Reconciling these perspectives is critical to moving forward. Pragmatically, this requires striking a balance between what can be done and living with the inevitable imperfections of what will remain. The significant uncertainties regarding the impacts of source management remain complicates efforts to strike the right balance. Fortunately, research continues to address these uncertainties. The following section provides a summary of recent research on the effects of source management on the source function, and on the plume response to source treatment.

Source Function

Sale and McWhorter (2001) evaluated how DNAPL depletion governs downgradient water quality by modeling heterogeneous distribution of DNAPL bodies in uniform porous media. A technique involving superposition of multiple analytical source terms allowed for analysis of DNAPL dissolution rates throughout complex sets of sparse DNAPL bodies in a uniform porous media (Type I Setting). A primary observation from this modeling effort was that most contaminant loading to groundwater plumes occurs at the upgradient edges of the DNAPL bodies. As long as the upgradient edges of DNAPL bodies remain, significant loading to downgradient plumes will continue.

From this observation, Sale and McWhorter (2001) concluded that “removal of the vast majority of DNAPL will likely be necessary to achieve significant near-term improvements in groundwater quality.” According to McWhorter and Sale (2003), the meaning of “significant near-term improvements in water quality” was achievement of the multiple order-of-magnitude reductions in aqueous concentrations that are typically required to attain risk-based MCLs. Similar limited reductions in contaminant loading with DNAPL depletion have been reported by Suchomel et al., (2007). Sale and McWhorter (2001) also recognized other potential benefits of partial depletion of DNAPL, including reduced source longevity, reduced site care requirements, and enhanced effectiveness of natural attenuation processes.

However, Rao and Jawitz (2003) contend that “in heterogeneous formations, significant contaminant flux reductions can be realized.” In support of this position they presented a one-dimensional analytical solution that addressed a system with uniform DNAPL in a nonuniform flow field (Type III setting). The modeling results indicated that DNAPL depletion on the order of 70 to 90 percent could yield reductions in loading to downgradient plumes by 70 to 98 percent.

McWhorter and Sale (2003) believe there is little difference between the conclusions of the two papers, if the goal is to attain MCLs throughout the source zone. In their analysis, Rao and Jawitz (2003) shifted the location of the envisioned water quality benefits from the source zone to the downgradient plumes. Specifically, they envision that upgradient reductions in contaminant loading will produce downgradient water quality improvements that result in stable or shrinking plumes. In practical terms, source treatment may be beneficial if it removes enough source material to allow a natural attenuation remedy to be protective, and/or to attain MCLs within a reasonable time frame. That decision will

largely be based on an estimate of the source strength after treatment, combined with estimates of the natural attenuation capacity of the downgradient aquifer.

Estimates of the achievable reductions in source strength are available from the laboratory studies of Suchomel et al. (2007). These researchers created sparse DNAPL zones in tanks filled with uniform sand (Type I Setting) and compared the effects of partial removal of the DNAPL in systems either dominated by DNAPL as a continuous phase in pools, or with DNAPL occurring primarily as isolated ganglia. They concluded that “in the ganglia dominated system greater than 70% mass (DNAPL) removal was required before measurable reductions in plume concentration and mass discharge were observed.” Furthermore, they observed that “for pool dominated source zones substantial reductions (>50%) in mass discharge were realized after only 50% mass removal.” Hence, it appears reasonable to conclude that fractional depletion of DNAPL will fall well short of attaining MCLs, but will yield reductions in downgradient loading to plumes.

Field measurements of the impacts of source treatment are also available (McGuire et al., 2006). Researchers evaluated water quality data from 59 chlorinated solvent sites before and after source depletion. Four source treatment technologies were included in the survey: chemical oxidation; enhanced bioremediation; thermal treatment; and surfactant/cosolvent flushing. Performance was evaluated by examining temporal groundwater concentration data before and after source remediation was performed. The results (Figure 15) indicated that “all four technologies have median concentration reductions of 88% or greater for the parent chlorinated volatile organic compound (CVOC). Approximately 75% of the source depletion projects were able to achieve a 70% reduction in parent compound concentrations. Based on current data, none of the 59 source depletion projects was able to meet maximum contaminant levels throughout the treatment zone for all CVOCs.”

Of course, these results are dominated by the impact on only one of the 14 compartments (the aqueous phase within the transmissive fraction of the source zone), because these are by far the most common measurements available. The masses remaining in other compartments may differ markedly between treatment approaches, but the failure to meet MCLs in source zone groundwater implies a continued need to manage the source due to the continued releases of contaminants to the plume.

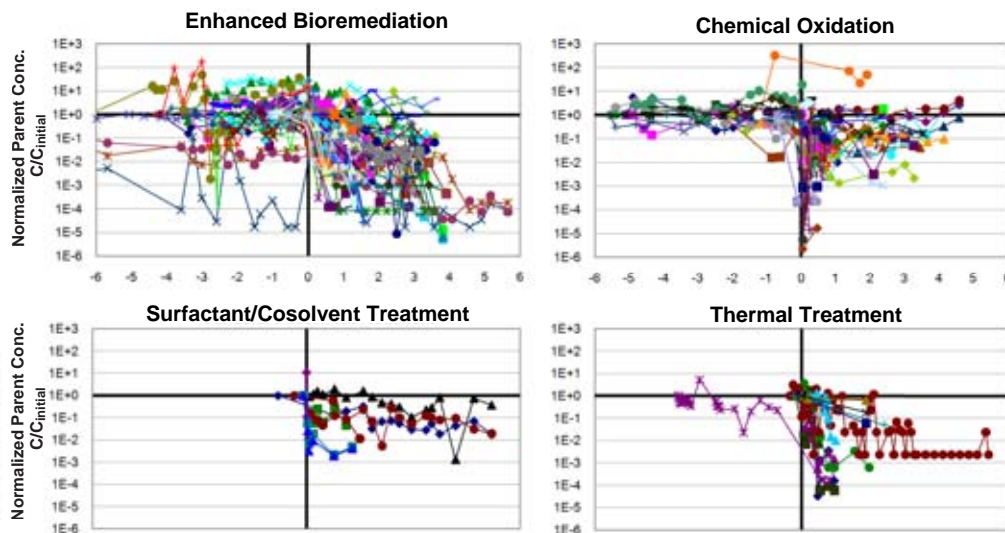


Figure 15 - Temporal Concentration Records for Wells at Source Depletion Sites (from McGuire et al., 2006).

Plume Response - Overview

Research has consistently shown that partial source DNAPL removal is unlikely to achieve MCLs (in the near term) throughout source zones (Sale and McWhorter, 2001; Rao and Jawitz, 2003; USEPA, 2003; NRC, 2005; McGuire et al., 2006; Suchomel et al., 2007). On the other hand, the research does suggest that attainable reductions in downgradient loading may yield beneficial improvements in downgradient water quality. The following explores the current state of knowledge regarding plume responses (plume function) to upgradient reductions in contaminant loading.

Plume Response and Attenuation - Wiedemeier et al. (1998) pointed out that select chlorinated solvents are attenuated via biotic processes. Typically this occurs at sites where reducing conditions exist in plumes due to the co-release of a fuel hydrocarbon. More recently it has been demonstrated that naturally occurring minerals can drive abiotic degradation of chlorinated solvents in plumes (Danielsen and Hayes, 2004). Active attenuation of dissolved phase chlorinated solvents, even at slow rates, can result in plumes that are naturally either stable or shrinking. Further, it can provide effective control of any residual contaminants stored in lower-permeability materials within the plume.

Given stable or shrinking plumes, two perspectives arise. First, in the absence of an expanding plume and with no current exposures to receptors from dissolved phase or

vapor plumes, actual risks to current receptors are likely to be negligible and there may be no need for further action. Second, the rate at which a plume is shrinking can be enhanced and/or its overall longevity can be reduced through reduction of the upgradient source. Chapelle et al. (2004) supported the latter point through review of data from a site in Kings Bay, GA. Results indicated that “source-area removal actions, particularly when applied to ground-water systems with a significant natural attenuation capacity, can be effective in decreasing the areal extent and contaminant concentrations of chlorinated ethene plumes.”

However, some chlorinated solvent plumes show little if any biotic attenuation, and therefore may be unacceptably large or still expanding. Large and expanding plumes are often problematic due to ongoing resource degradation and the potential for future impacts to receptors. Another potential problem in plumes with low degradation rates is that dissolved phase contaminants can accumulate in low permeability zones via diffusion. As discussed earlier, upgradient reductions in contaminant loading that reduce the dissolved phase concentrations in transmissive zones can also drive release of contaminants stored in plumes via desorption and/or back diffusion out of low permeability layers (Chapman and Parker, 2005).

Plume Response – Field Data - Back diffusion from low permeability layers in granular porous media can sustain plumes for decades after complete removal of sources (Sale et al., 2008). Field data from F.E. Warren Air Force Base (AFB), Wyoming (Figure 16) demonstrate the potential for sustaining plumes through back diffusion. An iron permeable reactive barrier was installed in 2000, decreasing the TCE concentrations at the barrier by multiple orders of magnitude, to values of less than 5 ug/L. However, after five years, TCE concentrations 40 and 60 feet downgradient of the barrier dropped by only one order of magnitude. The sustained concentrations of TCE downgradient of the barrier are attributed to desorption and back diffusion from low flow zones.

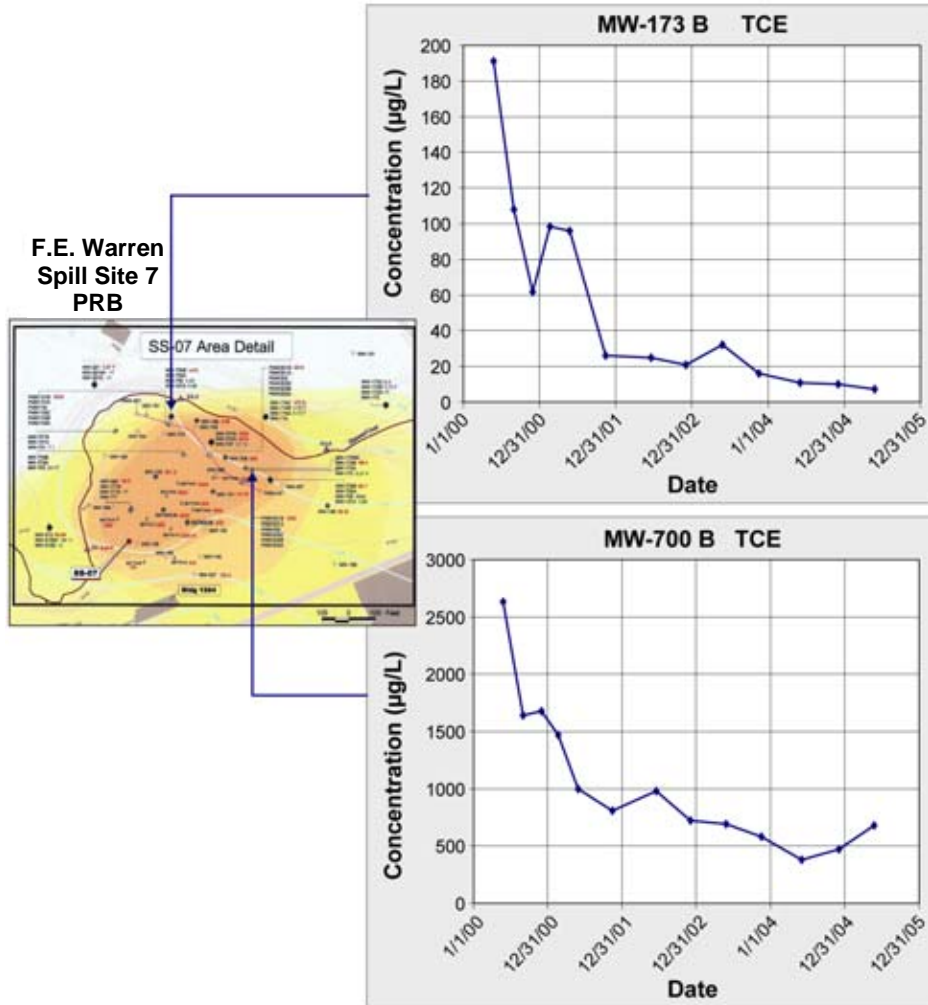


Figure 16 - Field data from F.E. Warren AFB (courtesy of F.E. Warren AFB and AFCEE).

Chapman and Parker (2005) studied an industrial site where a TCE source that started in the 1950s was isolated from the adjacent alluvial aquifer using sheet pile in 1994. Groundwater monitoring results from two wells located 330 m downgradient of the source in transmissive alluvium showed declining concentrations (slightly more than one order of magnitude) after the enclosure was built, but then concentrations appeared to level off. These data demonstrated that back diffusion was sustaining contaminant concentrations in the transmissive portion of the plume.

Detailed mass estimates indicated that approximately 3,000 kg of TCE was dissolved in the underlying aquitard in the first 280 m downgradient of the sheet pile enclosure, as compared to between 5,000 and 20,000 kg of DNAPL trapped within the enclosure. In other words, a new “source zone” (a weaker, non-DNAPL source) was created in the

downgradient plume by matrix diffusion downgradient of the DNAPL source. This new source zone represented between 15 and 60 percent of the remaining DNAPL mass at the site.

The two field sites demonstrate the importance of considering both the plume and source response when deciding how to manage sources. The mass stored in the plume and the rate of attenuation of that mass can largely determine the plume response to source depletion. If a relatively large fraction of the mass is in the plume, and if its attenuation is slow, even complete source removal may have relatively little effect on restoration time frames. On the other hand, if the attenuation rate is sufficient to handle any residual mass remaining in the source and plume after treatment, source depletion can greatly reduce the plume longevity and the costs for continued site management after active remediation. Thus, adequate characterization of the source – and the plume – is needed to predict the response of a given plume to a given level of source reduction.

Plume Response – Computer Models - Currently, a number of researchers are developing models that simultaneously address source strength and plume response as a function of time (e.g., Newell and Adamson 2005; Chapman and Parker, 2005; Falta, 2008; Sale et al., 2008). Each of these efforts has its merits and limitations. In all cases, the primary challenges include capturing the physics of the problem and acquiring the necessary inputs to run the models. The remainder of this section summarizes these different model development efforts.

Falta (2008) presents a new and powerful analytical solute transport model called REMChlor that allows the user to explore the effects of both source and plume remediation. The REMChlor model is useful for evaluating different scenarios, although one potential limitation is that it does not address contaminants stored in low permeability zones in the plume (Falta, 2005). A REMChlor simulation result is shown in Figure 17 for a hypothetical PCE release that is proposed to have occurred in 1975. This model scenario examined what would happen if site managers performed the following actions:

- A source remediation project was able to remove 90 percent of the DNAPL source mass in 2005, leading to a 90 percent reduction in the PCE mass discharge to the plume.
- Plume remediation was assumed to start in 2005, and extend for 20 years. The plume remediation assumes that the PCE and TCE decay rates can be enhanced over the first 400 m of the plume by the addition of an electron donor.

- A naturally-occurring aerobic treatment zone is assumed to extend from 400 m to 700 m, but the PCE and TCE are assumed to not degrade in this environment (where the DCE and VC are rapidly degrading).

The REMChlor model gave these results:

- By 2005, a large plume of PCE and its daughter products (TCE, DCE and VC) existed downgradient of the source (only the TCE component is shown in Figure 17).
- As shown in Figure 17, the leading edge of the TCE plume continues to advance for some time, despite the source and plume treatments. This continued expansion occurs because this contaminant mass is beyond the treatment zones at the start of remediation (referred to as “the horse has already left the barn” scenario by some).
- Note also that a small plume regenerates from the remaining source material once the plume treatment is stopped. Although it is weaker than the original plume, after 70 years the regenerated plume will be almost the same length as the original 2005 plume.

Newell and Adamson (2005) developed mass balance-based, planning level models to provide estimates of the reduction in remediation time frame (RTF) for a given amount of source depletion (source mass or flux reduction following intensive treatment). As a shared framework for assessment, the models use the time required to reduce the contaminant discharge from the source zone to below a mass flux goal as a metric. Impacts of source treatment on the RTF are assessed using a number of different types of source zone decay patterns, such as a *First-order Decay* model to represent a middle-of-the-road approach with a linear relationship between mass remaining and flux, or a *Compound* model to address situations where limited changes in the mass flux are achieved until a large percentage of the mass has been removed. These models are of interest in terms of providing:

- Absolute RTF estimates in years as a function of current mass discharge rate, current source mass, the remediation goal, and the reduction in discharge rate and source mass immediately after treatment, and
- Relative RTF estimates as a fraction of the remediation time frame for monitored natural attenuation (MNA) in the decision to proceed with source depletion or to use a long-term containment or MNA approach.

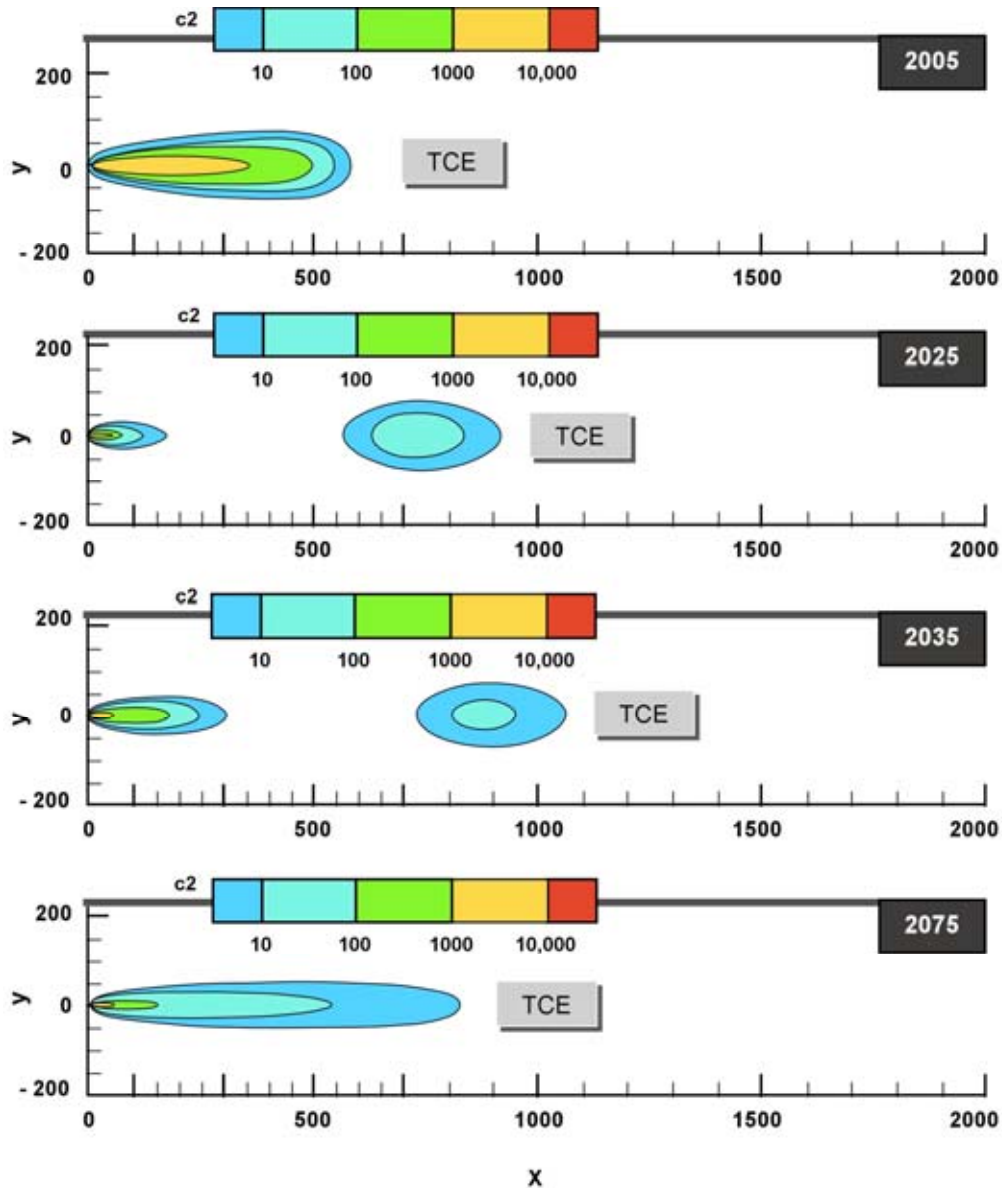


Figure 17 - Simulated plume concentration (ug/L) after 90% reduction in source mass + remediation of first 400 meters of plume, both occurring in 2005 (Falta et al., 2008). Dimensions x and y are in meters.

As an example of the first-order source decay scenario, a chlorinated solvent source in a homogenous aquifer (Type I) might require a remediation time frame of 184 years of mass discharge before concentration goals are achieved, due to slow source decay and the resulting decrease in flux as the source aged. If an initial source treatment (i.e., *in situ* chemical oxidation, enhanced bioremediation) successfully removed 70 percent of the source mass and reduced the mass flux by 70 percent, then the remediation time frame would decrease to 136 years (a decrease of 26 percent). This simple method

demonstrates that while source treatment can reduce the time to cleanup, the removal of significant amounts of source mass does not necessarily result in an equivalent reduction in the remediation time frame.

Note that this approach is focused on the source function and not the plume function, such that concentration goals must be attained at the downgradient edge of the source zone. However, the inclusion of a source decay term in effect incorporates the concept of storage and release of mass in low permeability layers within the source zone.

Chapman and Parker (2005) used a numerical model to simulate the plume response observed at the industrial site described above. This model, developed by Therrien and Sudicky (1996), is now referred to as HydroGeoSphere. Finite element numerical methods were employed to model a two-dimensional cross-section with a domain 300 m long and 15 m high. The domain was discretized using a total of 120,000 finite element hexahedral blocks and 241,602 nodes. Tighter vertical node spacing was used near the contact between the transmissive alluvium and underlying aquitard. Predicted water quality trends were similar to those observed in the field data. Extrapolation of the observed water quality data suggests that the current levels of TCE in the plume downgradient of the source enclosure will persist at levels an order of magnitude above the MCL for more than a century at this site. On a more positive note, the modeling work showed that (given sufficient domain discretization and model inputs) numerical models can be used to simulate simple scenarios of contaminant storage release processes in plumes.

More recently, Sale et al. (2008) presented an exact two-dimensional analytical solution of matrix diffusion between a transmissive layer overlying a stagnant no-flow layer. A DNAPL-like source located at the contact between the upper transmissive and lower stagnant layer was considered. The source discharged contaminant at a constant rate for five years. Downgradient water quality in analog wells was considered in wells located 1, 10, and 100 meters downgradient of the source while the source was active, and for an additional 15 years afterward. Typical flow conditions were considered, and sensitivity to retardation factors and rates of contaminant degradation was evaluated.

Results from the Sale et al. (2008) analysis are in Figure 18. In general, rates of cleanup of downgradient water quality improved after source removal, showing shorter half lives and lower retardation. In the best case (lower left-hand corner of Figure 18), downgradient water quality was below clean-up levels in the time it takes the water to travel from the

source to the wells. This outcome reflects limited accumulation of contaminants in the plume due to active contaminant attenuation via degradation. For the remaining scenarios, the greatest improvements in downgradient water quality occurred close to the source, with diminishing improvements as one progresses downgradient. These outcomes reflect the accumulating effect of back diffusion and desorption at larger downgradient distances. Furthermore, for the remaining scenarios the anticipated downgradient improvements in water quality (at 100 m, given complete source removal) were in the range of one to two orders of magnitude 15 years after removing the source.

Plume Response – Multiple Site Studies - It should be noted that previous compilations of concentration and plume length data for petroleum hydrocarbon releases have demonstrated a similar long-term persistence of plumes due to factors such as slow back diffusion and desorption (Newell and Connor, 1999). This behavior occurs as plumes age and sometimes transition into an “exhausted” state, such that the rate of change in concentration and plume size slows significantly even after depletion of NAPL. These studies provide clear evidence that this type of plume response is likely a widespread occurrence not restricted to chlorinated solvents.

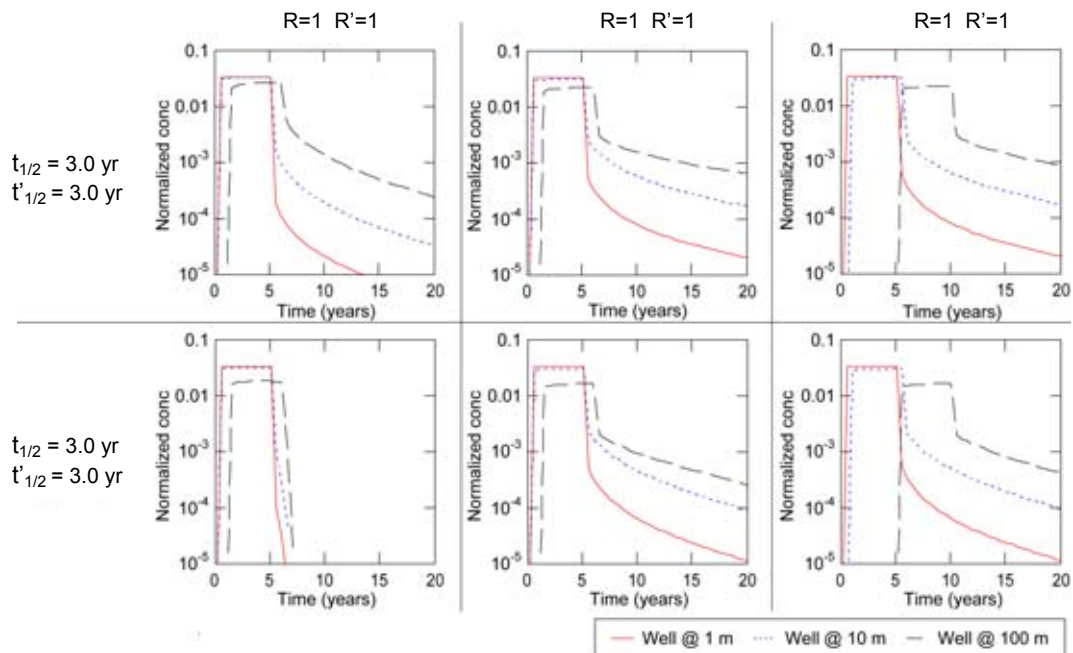


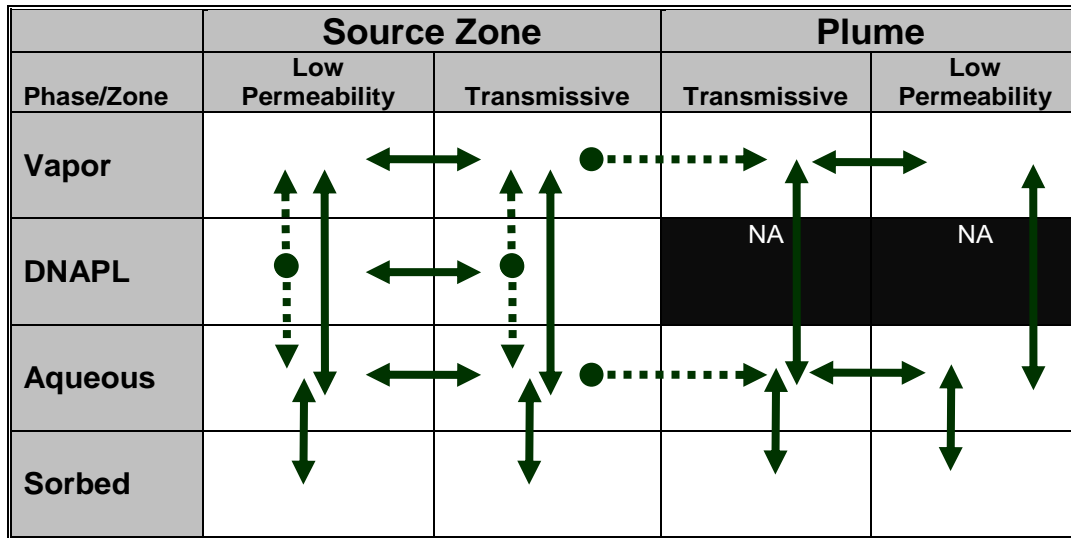
Figure 18 - Sensitivity concentrations in wells to contaminant half-life, retardation coefficient, and downgradient distance from source. Seepage rate is 0.3 m/day, the source is on from 0 to 5 years, and the wells have 3-m screens that are completed immediately above the sand-silt contact. R and R' are the retardation coefficients and k and k' are the half lives for the transmissive and stagnant layers, respectively. From Sale et al. (2008).

Summary

Plumes are inextricably linked to their sources. Given this linkage it follows that decisions regarding management of plumes are likely to involve decisions regarding management of sources. A common perception has been that removing the source will result in removing the plume (after several years of flushing), similar to a smoke plume disappearing once the source of the smoke is extinguished. Unfortunately, experience has made it clear that the relationship between sources and plumes is much more complicated, and that plumes can persist (at lower concentrations) long after their sources are depleted or contained. The degree to which plumes can persist is governed by site-specific attributes (e.g., geologic setting, hydrology, contaminant properties, biogeochemistry, and release volume) and the fact that chlorinated solvent sites evolve with time.

As a starting point this chapter advanced the concept that there are 14 compartments (8 in source zones and 6 in plumes) that can store and release contaminants. This concept builds on the recognition that there are *four phases* of concern (vapor, DNAPL, aqueous and sorbed) that can occur in transmissive zones with active groundwater flow, and in relatively lower permeability zones where diffusion may be the primary transport process. A key value of the 14 Compartment Model is that it advances a holistic view of the problem of chlorinated solvent releases. Historically, success with managing plumes (and source zones) often has been constrained by failing to take into account all of the consequential compartments and their interactions.

Clearly, chlorinated solvent releases evolve with time. In the initial state, the primary issue is presence of DNAPL in source zones. With time, DNAPL is depleted through dissolution and/or volatilization. However, plumes form and contaminants may be slowly driven into lower permeability zones via diffusion and slow advection, a process that “increases the entropy” (the disorder) of the site and makes it more difficult to clean up. At a middle stage, most if not all compartments are impacted. Finally, at the late stage, little if any DNAPL remains and the critical compartments are aqueous-sorbed phases in lower permeability zones, and large amounts of energy can be required to remove these contaminants quickly. A common feature at late stage sites is a large dilute groundwater plume with chlorinated solvents concentrations in the range of 10s to 100s of µg/L. Furthermore, at late stage sites little remains to differentiate source zones and plumes; rather what is left is a zone that has elements of a continuing source and elements of a plume.

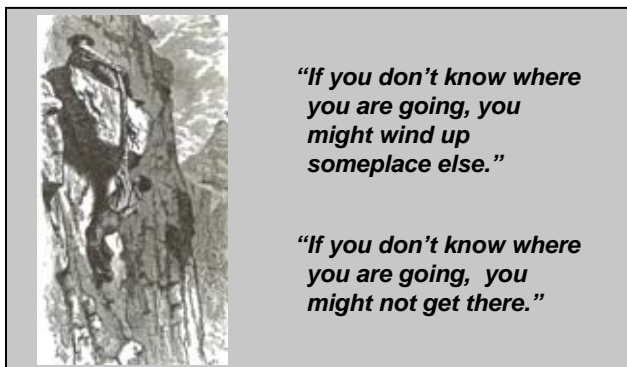


Given that almost all releases are now 30, 40 or even 50 years old, many sites have progressed to *middle* or *late* stages where contaminants are present in low permeability zones, both in the source and in the plume. The key concerns with contaminants in low permeability zones are their potential to sustain plumes for extended periods of time and their constraining effects on the benefits of technologies that solely address contaminants in transmissive zones. Flushing out the plume (i.e., pump-and-treat) is a slow, inefficient process when there are contaminants in the low-permeability compartment.

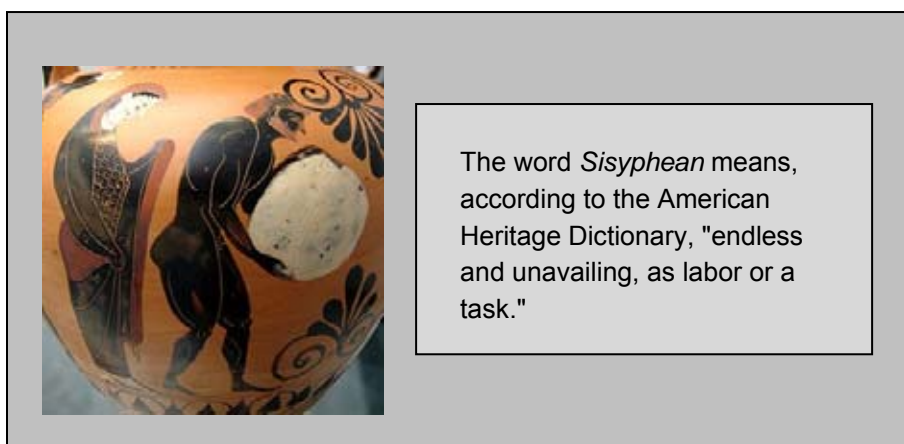
Over the past decade the effects of source control measures (depletion or containment) on plumes has been the focus of rigorous debate and research. It is now clear that source treatment will reduce the ultimate total mass in downgradient plumes, and will likely result in reduced plume extent and/or longevity. However, in most instances it is likely that contaminants will remain and persist for extended periods, leading to a sense that no action will get a site to closure. Reconciling these perspectives is critical to moving forward in risk management and site remediation. A pragmatic approach would be to strike a balance between what can be done and living with the inevitable imperfections that remain.

Section 3 - Formulating Objectives

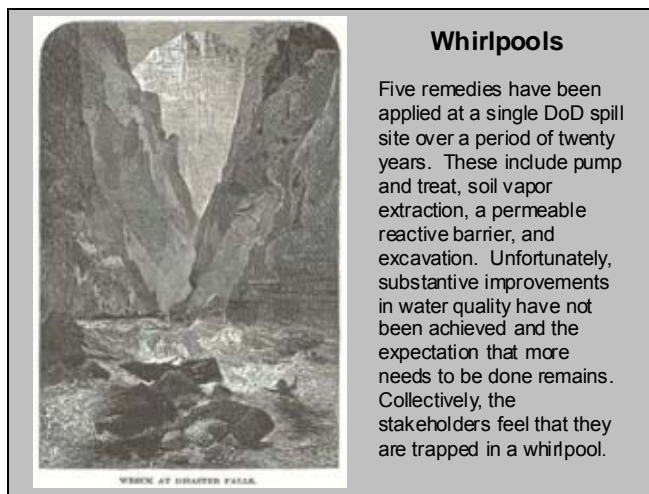
In almost any initiative, success is far more likely if you have a clear idea of what you are trying to accomplish. In the words of Yogi Berra:



Berra’s observation is relevant to selecting remedies for chlorinated solvent releases. The absence of well-defined, agreed-upon objectives among site stakeholders has been a common problem. A case in point is the fact that achievement of stringent concentration-based cleanup standards for contaminants in groundwater (e.g., MCLs) has proven elusive at most remediation sites (USEPA, 2003; NRC, 2005), even when the best available demonstrated technologies have been used. At some of these sites, a conflict can result between stakeholders about the remediation process: some feel remediation is incomplete and therefore additional remediation efforts are needed, while others feel that the entire remediation process is a never-ending Sisyphean task (see box below) that provides little additional benefit to society. Regrettably, a sense of failure can exist even in cases where important progress has been achieved, such as stabilizing plumes, mitigating exposure pathways, and/or restoring beneficial land use.



On one hand it can be argued that we are making incremental progress. On the other hand it can be argued that we are trapped in a whirlpool where there is little clarity as to where we are headed or when we will get out.



Pondering the importance of clear remediation goals, NRC (2005) states:

“Failure to explicitly state remedial objectives appears to be a significant barrier to the use of source remediation technologies.”

and

“The vagueness with which objectives for remedial projects are often specified can preclude effective decision making with regards to source remediation”

Going further, NRC (2005) recognizes that the parties making decisions often have multiple and potentially competing objectives and that the relative importance of each objective can vary widely between decision makers. An example of potentially competing objectives is near-term attainment of MCLs in a groundwater plume under a residential neighborhood and minimizing interruptions to daily life in the neighborhood. At the extreme, near-term attainment of MCLs might require excavation which could cause unacceptable interruption to daily life in the neighborhood. At the other extreme, not addressing the fact that the plume is there may put some residents at risk.

When uncertainties in remediation technology performance are added to the decision process, it is not surprising that NRC (2005) observes a *“widespread problem of vaguely formulated remedial objectives.”* Building off NRC (2005) the opportunity we have now at chlorinated solvent sites is to do a **better job of establishing objectives** that effectively

address the needs of the various parties. This section presents key concepts and tools for establishing beneficial and attainable objectives for chlorinated solvent releases.

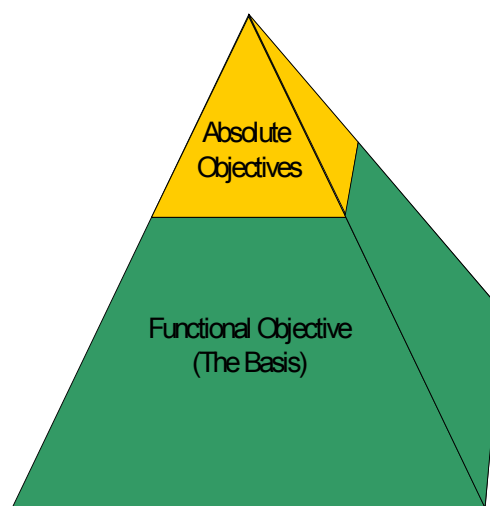
As a first step, objectives are considered in terms of being “absolute” or “functional.” This is followed by a shopping list of absolute and functional objectives that are common to many sites and can be used as a starting place for developing specific objectives at a specific site. Subsequently, in Section 5, Absolute and Functional objectives are used to develop and then improve packages of remedial measures designed to holistically reflect the need of the stakeholders.

Types of Remediation Objectives

Understanding that there are different types of objectives leads to clarity in understanding what needs to be accomplished. Good objectives have two essential attributes: they are both beneficial and attainable. The importance of good objectives can be illustrated by considering the limited value of bad objectives - there is little reason to set an objective that has no benefits and/or is unattainable. Finally, objectives need to reflect the needs of all impacted parties. So long as a consequential need of any party is left behind, final resolution of a site is likely to be elusive. This section expands on these key themes.

The National Research Council panel that developed the NRC’s Source Document (NRC, 2005) included experts in a wide range of fields, including experts in the area of decision making. During their deliberations, an important concept about two different types of objectives was integrated into their work and ultimately into their final report.

Absolute objectives reflect broad social values such as protection of human health and the environment. Unfortunately, absolute objectives are often so broad that they lack the specificity needed to design site remedies. In contrast, **functional objectives** are specific, quantifiable, and verifiable. For example, mitigating potential adverse health impacts is an *absolute* objective, while achieving MCLs in groundwater at a specific point in a plume at a specified time is a common *functional* objective. Absolute objectives drive the selection of functional objectives,



and functional objectives are typically the basis for implementing remedial measures. If a project is successful, functional objectives have outcomes that lead to attainment of the desired absolute objectives.

In addition, absolute objectives are largely irrevocable whereas functional objectives are fungible (functional objectives can be modified and changed to adapt to new knowledge and/or changing site conditions). Few would advocate stepping away from the absolute objective of protecting human health and the environment. In contrast, a regulatory near-term attainment of MCL at all points could be modified to near-term attainment of MCLs at select points and long-term attainment at all points.

Fungible - may be used in place of another equal part in the satisfaction of an obligation.
- Webster's Collegiate Dictionary

Attributes of Good Functional Objectives

There are a number of different decision-making systems used in management sciences and business that present the attributes of good objectives. For example, the SMART mnemonic has been used in project management at the project objective setting stage since 1981:

- **Specific**
- **Measurable**
- **Attainable**
- **Relevant**
- **Time-bound**

Building on this type of system, we have developed the following six attributes of a good functional objective for remediation projects. The first two are considered essential.

1. *Beneficial.* An effective remediation objective results in a net environmental benefit at the site being managed. In other words, the end-state is some type of improvement over existing conditions or the "no-action" alternative. The most highly beneficial objective would be complete restoration of the contaminated soil and groundwater at the site. This objective, while having

significant environmental benefits, has been very difficult to achieve at chlorinated solvent sites. Therefore, the attainability of a remediation objective is an important attribute.

2. *Attainable.* To many, the flip-side of “beneficial” is “attainable.” However, there are a myriad of remediation and site management alternatives that are both attainable and result in significant environmental benefit. Stake holders need to consider the attainability of any remediation alternatives being considered by asking “Can this be achieved, or will we be disappointed?” Implementing beneficial but not attainable remediation goals is disruptive to the entire remediation process and results in unrealistic expectations about the outcome of a remediation project.
3. *Verifiable.* One of the key points about the observation approach discussed in FAQ 24 (*Frequently Asked Questions Regarding Management of Chlorinated Solvents in Soils and Groundwater*) is that stakeholders should establish key parameters for observation, measure them, and compare predicted values to measured values. Therefore, any remediation objective needs to have a quantifiable, relatively unambiguous metrics to determine if progress is being made, and ultimately, if the objective has been achieved. Note that measuring remediation progress can be difficult considering the scatter in many of the environmental datasets that are associated with remediation sites. Stakeholders should develop objectives that can be verified even with scatter in the data.
4. *Adaptable.* Because of the uncertainties associated with site data, remediation technology performance, and other aspects of the remediation process, stakeholders need objectives that can be flexible and iterative if new information surfaces during remediation. FAQ 24 of the FAQ document stresses the importance of adaptive site management approaches such as flexible Records of Decision, treatment trains, and constant optimization of remedial systems and monitoring networks. In the end, stake-holders need to be flexible, iterative, and embrace adaptability during the remediation process.

5. *Consistent with the needs of the community.* The community is an important stakeholder, either as a direct member of the decision-making group, or as an implicit partner in site decisions. A number of guidance documents developed by regulators, industry, and government groups emphasize that the needs of the local communities need to be considered in developing remediation objectives.
6. *Collaborative.* Developing remediation objectives should be a collaborative process, where different stakeholders discuss, process, evaluate, and then decide about the correct remediation objectives for a site. Having the right information about benefits, attainability, verification, and community needs is crucial to making this collaborative process work. One common pitfall is the “immovable object” vs. “irresistible force” factor, where statutory objectives (such as rapid, complete restoration of groundwater) are at odds with technical factors (such as the inability of any technology to reach this goal). Stakeholders need to account for these factors and then collaborate to overcome decision-making roadblocks and impediments.

Common Objectives for Remediation Projects

Through this project and participation in Interstate Technology & Regulatory Council (ITRC) committees, the authors have noted several *absolute objectives* for historical releases of chlorinated solvents that are commonly prescribed for cleanup projects:

- *Protection of human health and the environment*
- *Conservation of natural resources*
- *Mitigation of adverse community impacts*
- *Minimizing the burden of past practices on future generations*
- *Performing work in an efficient and cost-effective manner.*

Similarly, common *functional objectives* are presented in Table 3. Many of these have an origin in specific regulatory programs (such as Superfund), expert panels (such as USEPA, 2003), and remediation movements (such as the Sustainable or Green Remediation). A review of the basis for noted absolute and functional objectives is provided at the end of this section. For any given site, both absolute and functional objectives should be tailored to the needs of the parties involved.

Table 3 – Examples of common functional objectives

Risk
Prevent active adverse human exposure via groundwater or soil gas
Prevent active ecological exposure via groundwater or soil gas
Prevent adverse worker-related exposures via soil, groundwater, and/or vapor
Avoid actions that have the potential to increase risk
Extent
Prevent expansion of source zones and plumes
Reduce the extent of source zones and plumes
Longevity
Reduce the period in which immobile contaminants in source zones will provide persistent releases to groundwater and/or soil gas
Reduce the period in which immobile contaminants in plume will provide persistent releases to groundwater and/or soil gas
Regulatory
Comply with local, state, and federal regulations
Community
Address adverse (non-health) impacts to communities
Land use
Restore beneficial use of impacted lands
Economic
Select actions that have reasonable capital costs and life cycle cost
Avoid undue interruptions to communities, government, and industry activities
Redress adverse impacts to property values
Sustainability
Select measures that have a net positive environmental benefit
Progress to a state in which passive remedies will be sufficient to address residual impacts
Enhance the effectiveness of complementary technologies
Implementability
Select measures that have a low probability of failure in the implementation phase
Resource Conservation
Limit future degradation of resources
Restore impacted groundwater to standards required for beneficial use
Protect sensitive biological habitat

Summary of Objectives from Key Regulatory and Technical Sources

USEPA's Nine Criteria

The first comprehensive guidelines for selecting remediation approaches were developed as part of the National Contingency Plan (NCP) for the Superfund program in 1982. Under the Superfund program, remedial alternatives are compared to one another using nine different criteria divided into three different roles in the decision-making process.

There are two “threshold” criteria that must be satisfied, unless the site managers receive a specific waiver from the U.S. EPA:

- *Overall protection of human health and the environment.*
- *Compliance with applicable or relevant and appropriate requirements (ARARs) under federal environmental laws and state environmental or facility siting laws.*

There are five “balancing” criteria used to compare the advantages and disadvantages of the criteria:

- *Long-term effectiveness and permanence.*
- *Reduction of toxicity, mobility, or volume through treatment.*
- *Short-term effectiveness.*
- *Implementability. The ease or difficulty of implementing the alternatives must be assessed.*
- *Cost. The types of costs that shall be assessed include the following: Capital costs, including both direct and indirect costs; (2) Annual operation and maintenance costs; and (3) Net present value of capital and O&M costs.*

Finally there are two “modifying” criteria that are designed to provide states or local communities a voice in the overall decision-making process:

- *State acceptance.*
- *Community acceptance.*

Since 1982, this decision-making process has developed with several typical practices. For example, consideration of the “Overall protection of human health and the environment” criterion has typically been conducted using a human health risk assessment. Compliance with ARARs has focused on meeting MCLs in groundwater, among other quantitative standards (NRC, 2005). In particular, MCLs can be a confusing objective, as the relationship between monitoring well concentrations and source remediation is very complex (NRC, 2005).

Risk-Based Corrective Action (RBCA)

In the late 1990s, “Risk-Based Corrective Action” (RBCA) became an important decision-making component of many remediation programs. The RBCA process was formalized in the American Society for Testing and Materials (ASTM) RBCA standard (ASTM, 1998). RBCA and RBCA-like programs were adopted by many regulatory groups, including over 40 state-level programs which had been charged with remediating leaking underground

storage tanks. In other states, such as Texas, RBCA concepts were integrated into the full range of remediation activities regulated by the state, including the State Superfund Program, the Voluntary Cleanup Program, and the Texas Petroleum Storage Tank program.

The RBCA programs focused on eliminating or controlling the risk at a site, not on the presence of the contaminant itself. RBCA programs provided a standardized way to collect necessary site data, identify exposure pathways, and then, using dose and transport equations, back-calculate site cleanup standards for all affected media. The site managers would then implement remediation projects to meet these goals. However, most RBCA programs also allowed for control of the risk using institutional, engineered, or natural controls at a site that would leave the contaminants in place but interrupt the risk pathway of concern.

2003 EPA Expert Panel on DNAPL

In 2003, the U.S. EPA issued a report in which an Expert Panel chaired by Mike Kavanaugh and Suresh Rao was asked to examine four specific issues regarding DNAPL source-zone treatment and management. These issues were:

- Status of technology development and deployment for DNAPL source remediation.
- Assessment of source remediation performance goals and metrics.
- Evaluation of costs and benefits of source remediation.
- Research issues and needs.

The Panel evaluated the decision to undertake source zone remediation, and concluded that the decision-making process is based on highly site-specific conditions and criteria, and that numerous stakeholder factors needed to be considered. The Panel went on to say:

“The Panel concluded that new approaches to this decision process are needed. Therefore, the Panel considered two distinct options for developing an improved decision analysis framework: one based on a qualitative, semi-empirical analysis, and the other based on a quantitative model based analysis. The Panel recognizes that neither of these options has been formally used at DNAPL sites for decisions on whether to implement source-depletion technologies, but the Panel urges EPA to consider the utility of qualitative approaches as a

screening level tool for evaluating the appropriateness of source depletion compared to containment...”

A modified version of the Qualitative Decision Guide was incorporated into FAQ 21 of the FAQ document. This chart outlined six criteria for evaluating the need for source treatment. Noted criteria include: 1) Reduce potential for DNAPL migration as a separate phase; 2) reduce source longevity and long-term management requirements; 3) reduce mass flux; 4) near-term attainment of MCLs; 5) regulatory requirement; and 6) intangibles. Users were asked to select if each criteria (with additional sub-criteria for some of the six top-level criteria) resulted in “more need,” “neutral,” or “less need” for source treatment.

Under this system a wide range of factors (11 total subcriteria) are evaluated to determine if source treatment is an appropriate response at a site, or if some type of containment remedy is a better selection.

National Research Council and Remedial Objectives

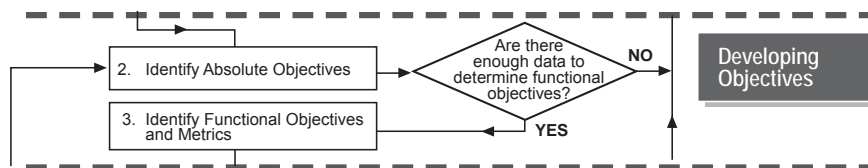
The National Research Council (2005) reviewed objective settings at a number of remediation sites and concluded that the objectives being used “made it difficult to determine the ‘success’ of projects under any consistent definition.” They also focused on the differences between absolute objectives (an objective important in and of itself, such as protecting human health) and functional objectives (a means to get to an absolute objective). Based on their observations and findings, the NRC made the following recommendations:

- Remedial objectives should be laid out *before* deciding to attempt source remediation and selecting a particular technology;
- A clear distinction between functional and absolute objectives is needed to evaluate options;
- Each objective should result in a metric, that is, a quantity that can be measured at a particular site in order to evaluate achievement of the objective;
- Objectives should strive to encompass the long time frames which are characteristic of many site cleanups involving DNAPLs.

The NRC went on to develop a Remediation Decision Process in the form of a flowchart that integrated these key recommendations into a single system. The flowchart is comprised of these major steps (see FAQ 23):

- Understanding the problem (collect site data and develop a site conceptual model);
- Developing objectives (identify absolute and functional objectives);
- Resolving what is attainable (determine if enough data are available, identify potential technologies);
- Selecting remedies and performance metrics (design and implement technology);
- Verify desired performance (determine if objectives have been met; determine if there are sufficient data).

The “developing objectives” portion of the flowchart (shown below) emphasizes the distinction between functional and absolute objectives, and considers the question of whether there are enough data to determine the functional objectives.



Sustainability Remediation Movement

Over the past two years, a new decision-making framework has begun to develop under the umbrella of “Sustainable Remediation” (SURF, 2009). One workgroup, the Sustainable Remediation Forum (SURF), as of February 2011, has met sixteen times to discuss, evaluate, and start to institutionalize sustainability concepts into remediation.

Because it is such a new field, there is no formal definition of sustainable remediation, just different groups implementing a variety of sustainability programs. Most programs seem to focus on calculating and then weighing different sustainability metrics, metrics that are not typically considered or are underweighted in current remediation decision making. Examples of “sustainability metrics” include such factors as:

- Carbon footprint (both total emissions and pounds of CO₂ emitted per pound of contaminant removed)
- Energy use
- Materials and resource use
- Worker safety/accidents

Groups such as SURF are trying to promote acceptance of sustainability concepts into remediation decision making, and make the case that sustainable remediation is a more holistic way to determine the appropriate remediation response. A survey of environmental regulators conducted by the SURF group, however, suggested that overall, regulators are generally more skeptical of the sustainable remediation movement, as it can be used as a way to steer remediation decision making to more passive, less energy intensive, and slower remediation technologies.

Section 4 - Resolving What is Attainable

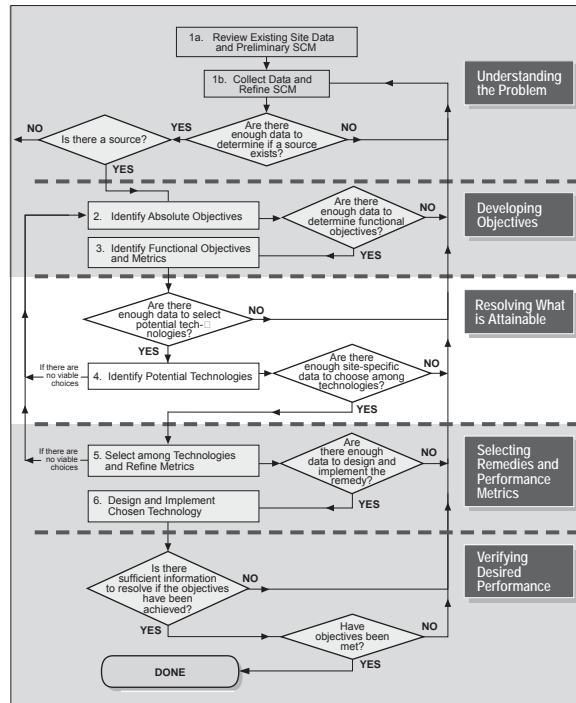
Overview

Over the past 40 years a diverse set of technologies have been advanced for managing subsurface releases of chlorinated solvents. This has come about through federal research initiatives (e.g., ESTCP/SERDP), industry research efforts (e.g., The University Consortium²), and implementation of remedies at thousands of sites. Through these investments we now largely understand both the performance and cost of a diverse set of proven technologies.

Furthermore we can now ask ourselves *a priori* which technology,

or suite of technologies, is best suited to address our objectives. If no option is likely to achieve our objectives, NRC 2005 suggests we revisit our functional objectives and resolve what is attainable. Revisiting functional objectives is clearly a far better alternative than proceeding with a remedy that is unlikely to achieve the targeted objectives. The process of screening technologies and resolving what is attainable is highlighted in the adjacent flow chart adapted from NRC 2005.

The focus of this section is to advance our current understanding of what proven technologies do and, equally importantly, do not do. This forms a foundation for moving through the third step in the NRC process – resolving what is attainable. Our technology review relies on the 14 Compartment Model introduced in Section 2.



² Formerly, the University Consortium for Chlorinated Solvents in Groundwater. Currently, the University Consortium for Field-Focused Groundwater Contamination Research.

Our consideration of what technologies don't do is not intended to discourage their use, but merely to encourage realistic expectations. Furthermore, we wish to emphasize the value of doing what is beneficial and attainable while (if necessary) planning to live with what may remain. Having a clear *a priori* understanding of outcomes is critical to making sound decisions. A primary theme advanced in this section is that we need to move forward from the approach that has often been used in the past - to try a remedy, only to find that it doesn't meet our objectives or significantly reduce the future site management requirements. Today we know enough that we can move beyond the whirlpool of application followed by perceptions of failure and unanticipated needs to do more.

Proven Technologies

This section addresses proven treatment technologies using the 14 Compartment Model. Quoting Cherry et al. 1996, a proven technology is "*a technology for which:*

- A considerable base of experience and success currently exists
- Commercial organizations offer the technology in the market place and
- The performance (and cost) of the technology is reasonably predictable."

Our analysis has not been extended to emerging or experimental technologies. Based on the definition above, emerging or experimental technologies generally lack a base of experience and success, organizations do not offer the technology, and/or processes are not well understood relative to performance and cost. Emerging and experimental technologies are seen as being best suited to situations where the primary objective is advancing new technologies or dealing with intractable conditions at a site. This statement is not intended to discourage advancement of emerging or experimental technologies or site-specific testing, but only to acknowledge the uncertainties inherent in new processes.

Technology Evaluation

For each technology in this section the following are addressed:

- Process components
- Governing processes
- Anticipated performance
- Niche

- Favorable attributes
- Limiting attributes

Our evaluation begins with treatment technologies. Treatment technologies are generally preferred due to their permanence. General categories of proven treatment technologies include:

- Recovery
- *In situ* degradation

Next, containment technologies are addressed. At some sites, containment approaches may provide the only practical near-term means of addressing impacts to human health and/or the environment. However, the long-term aspects of containment and lack of permanence generally make containment a second choice. Containment approaches considered include:

- Physical barriers
- Hydraulic barriers
- Permeable reactive barriers

The 14 Compartment Model is used to describe how technologies affect contaminant concentrations in each of the 14 compartments and how they affect contaminant fluxes between the compartments. As a first step, a rigorous development of the 14 Compartment Model for screening technologies is provided for pump and treat. Subsequent technology descriptions follow the approach developed for pump and treat.

We recognize that there are more technologies than those described herein, and for “other technologies” we encourage readers to follow our approach and develop their own analysis. Furthermore, we wish to encourage users of this document to consider other sources of information regarding performance of remedial measure. One of the most promising sources of additional information is ESTCP project ER-200424 - Development of a Protocol and a Screening Tool for Selection of DNAPL Source Area Remediation. A final report for this project is anticipated in 2011.

Treatment Technologies

Overview

Over the past 40 years, treatment technologies for chlorinated solvents in subsurface setting have evolved dramatically. Prior to the late 1970s a common response to chlorinated solvents in groundwater was to abandon impacted wells and/or wellfields and drill new wells in an uncontaminated portion of an aquifer.

By the 1980s and 1990s, the primary focus became recovery of contaminants via extraction of water, NAPL, and/or soil gas. Much like petroleum production, these technologies are predicated on the principle of recovery. With time, field data led to the recognition that slow rates of contaminant production often yielded slow progress. This led to advancement of more intensive recovery technologies, including surfactant-cosolvent flushing (e.g., Simpkin et al., 1999) and steam flushing (e.g., Davis 1998). In large part these technologies were predicated on enhanced oil recovery technology developed for the petroleum industry. Due to a combination of high cost, limited effectiveness, potential adverse impacts, and/or emergence of preferred alternatives, neither surfactant-cosolvent flushing or steam flushing have been broadly adopted (to date) as solutions for releases of chlorinated solvents. For each, the number of full-scale applications (excluding pilot studies) is limited to a handful of sites.

In the 2000s the remediation industry began a shift toward technologies that drive *in situ* degradation of chlorinated solvents via chemical, biological, and/or thermal processes. Each of these approaches has seen tens to hundreds of applications as full-scale remedies at chlorinated solvent sites. At the same time, older recovery-based processes, including pump and treat, excavation, and soil vapor extraction, continue to see wide use.

As a final introductory comment, the text below relies on generalizations regarding conditions at sites and performance of technologies. The technology performance information presented here is not intended to be taken as hard and fast rules that are applicable to all sites under all conditions. Rather, the information below is based on the author's general experience of contaminant distribution and technology performance. We envision that users of the 14 Compartment Model and the system below will customize the contaminant distributions, transfer of mass between compartments, and technology

performance to meet site-specific conditions and the user's own experience with remediation.

Furthermore, we assume that the technologies are "well implemented". As with all assumptions and generalizations there can be important exceptions. The physical characteristics of your site, your objectives, and/or the site-specific performance of a given technology may be different from what is considered herein. We encourage readers to think carefully about the unique aspects of their sites, their site-specific goals, and their own knowledge of how technologies work.

Recovery Technologies

Today's primary suite of recovery technologies for chlorinated solvents includes pump and treat, excavation, and soil vapor extraction.

Pump and Treat (for depletion vs. containment)

Description - Pump and treat involves extraction of groundwater using conventional wells or drains followed by *ex situ* treatment of groundwater. *Ex situ* treatment of groundwater typically involves either dedicated onsite treatment systems or discharge to a local publicly owned treatment works (POTW). A comprehensive review of pump and treat is provided in (USEPA, 1996).



Driscoll (1986)

Governing Processes - An early conceptual model for pump and treat was that the subsurface was analogous to a large underground storage tank. Removing the contamination was a simple matter of emptying the tank. Unfortunately, the dissolved phase in transmissive zones (the primary target of groundwater extraction) is often a minor fraction of the total contaminant mass that needs to be addressed. Depleting the dissolved phase in a transmissive zone (by removal or *in situ* degradation) often results in slow (and potentially chronic) recontamination from vapor, sorbed, NAPL phases in

3-4	99.9% or better
2	99 %
1	90%
0	9% or less

transmissive zones and/or from vapor, NAPL, aqueous, and sorbed phases in low permeability zones.

Anticipated Performance – Figure 19 maps the effects of pump and treat in a source zones using the 14 Compartment Model. An **Order-of-Magnitude (OoM)** black-gray-white color scale (with numerical values) is provided for each compartment to characterize anticipated OoM reductions in contaminant concentrations after a typical period of implementation. In addition, fluxes between compartments are shown. Note the anticipated performance is thought to reflect conditions after several years (e.g. 3-10 years). Typically, even longer periods of operations (e.g. multiple decades) would improve the technology ratings.

Orders of Magnitude (OoMs)

An Order of Magnitude (OoM) is a factor of 10 change in a variable. For example, if a remediation technology reduces the dissolved phase concentration of TCE by one OoM, then the concentration is 10 times lower, equivalent to a 90% reduction. Two OoMs thus represents a reduction in concentration of 99%. The concept of OoMs is an important short hand for evaluating remediation performance in the 14 Compartment Model. We use the concept of OoMs because chlorinated solvent concentrations in groundwater typically span several orders of magnitude, and are generally represented best by a log-normal statistical distribution. OoMs are used to describe the change in concentrations, contaminant mass, and mass discharge.

Summary:

- 0 OoM: 9% or less reduction in concentration, mass, or mass discharge
- 1 OoM: 90% reduction in concentration
- 2 OoM: 99% reduction in concentration
- 3 OoM: 99.9% reduction in concentration

Pump and Treat 14 Compartment Performance Chart

Phase / Zone	Source Zone		Plume	
	Low Permeability	Transmissive	Transmissive	Low Permeability
Vapor	0- Extraction of aqueous phase contaminants from the transmissive zones is likely to have little effect on vapor phase contaminants.			
DNAPL	0 - DNAPL if present in large amounts has the potential to be a long term source.			
Aqueous	0- Depletion of aqueous phase from transmissive zones will cause slow release from low permeability zones.	2 - Groundwater extraction from the source zones will cause direct depletion of aqueous phase in transmissive zones.	1 - Elimination of upgradient aqueous phase loading can yield a 1 -2 OoM reduction in downgradient aqueous concentrations.	0 - Depletion of aqueous phase from transmissive zones will cause slow release from low permeability zones.
Sorbed	1 - Depletion of the aqueous phase in transmissive zones will drive release of sorbed solvents. Note for select sorption processes desorption can be a slow process.			

Figure 19 – Pump and Treat performance mapped using the 14 Compartment Model. Arrows indicate potentially induced releases from other compartments. The dashed arrows indicate a speculative response depending on site conditions. Note that greater depletion could be achieved through longer periods of pumping. The above is intended to be reflective of several years (versus several decades) of pumping.

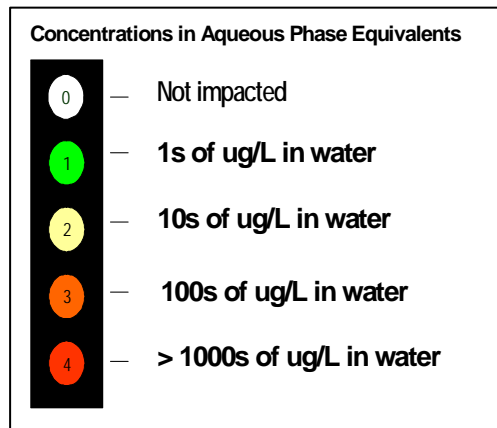
General insights from mapping the performance of pump and treat include:

- The aqueous phase in the transmissive portion of the source zone (light gray boxes) will be directly depleted through groundwater extraction. This can effectively eliminate the aqueous phase flux to the downgradient transmissive zones in the plume.
- Three compartments (dark gray) will see secondary effects from depletion of the aqueous phase in the source. This includes a potential 1 OoM reduction in concentrations in the aqueous phase in the plume. Note that this and other rules presented in this section are a general statement and performance at individual sites may vary significantly.
- Six compartments (dark gray) will see limited secondary effect. These compartments are likely to sustain the aqueous phase in transmissive zones for an extended period.

- Last, four compartments (black) are anticipated to be largely unaffected by a pump and treat system.

Figure 19 and the above insights illustrate why pump and treat has often been an ineffective means of depleting subsurface releases of chlorinated solvents. As stated in the introduction to this section, this technology analysis (and all subsequent analyses) involves generalizations that may not be universally true. Readers are encouraged to adjust these interpretations of technologies to the specific conditions they are addressing at individual sites.

Niche - A potentially promising niche for pump and treat is fractured rock settings with low matrix porosity (Type IV setting – See Section 2). In this setting contaminants will largely be absent from the matrix blocks (low permeability zones) and pumping can induce high rates of flow through interconnected fractures (transmissive zones). A portrayal of a plausible distribution of chlorinated solvents in a



late-stage Type 4 setting is presented in Figure 20. A primary assumption of Figure 20 is that contaminants stored in dead end fractures are not significant.

Zone/ Phases	Source Zone		Plume	
	Low Permeability	Transmissive	Transmissive	Low Permeability
Vapor	0	1	1	0
DNAPL	0	0		
Aqueous	0	2	1	0
Sorbed	0	2	1	0

Figure 20 – Plausible distribution of chlorinated solvents in a late stage Type 4 setting (fractured rock with low matrix porosity)

An OoM approach is employed in Figure 21 to anticipate the effects of employing source zone pump and treat in a late-stage Type IV setting. The approach involves subtracting the OoM “before” concentrations from the OoM technology (“Tech”) performance rating seen in Figure 19 to estimate “after” treatment concentrations. Results less than 1 are

reported as 0. The circled “after” results indicate that the anticipated outcome is “not impacted” in all but the vapor phase and transmissive zone sorbed phase. By itself this might be a sufficient remedy. Alternately, a vapor extraction system could be combined with pump and treat to address the anticipated post-treatment vapor phase contamination. Examples of combined remedies are discussed in Section 5 of this document.

Zone/ Phases	Source Zone						Plume					
	Low Permeability			Transmissive			Transmissive			Low Permeability		
	Before	Tech	After	Before	Tech	After	Before	Tech	After	Before	Tech	After
Vapor	0	0	0	1	0	1	1	0	1	0	0	0
DNAPL	0	0	0	0	0	0						
Aqueous	0	0	0	2	2	0	1	1	0	0	0	0
Sorbed	0	0	0	2	1	1	1	1	0	0	0	0

Figure 21 – Anticipated outcome from source zone pump and treat in a late-stage Type IV setting. Boxes in the “Tech” columns show estimated performance of remedial action based on the number of OoMs of concentration reduction. “After” values equal “before” values minus “Tech” values.

Further insight regarding source zone pump and treat can be gained by repeating the Figure 21 analysis for a middle stage Type III setting (e.g., heterogeneous alluvium with less than half of the original DNAPL release remaining). This is done in Figure 22 using the same technology ratings. The results suggest that source zone pump and treat in a middle-stage Type III setting could leave unacceptable contaminant concentrations in all 14 compartments.

Zone/ Phases	Source Zone						Plume					
	Low Permeability			Transmissive			Transmissive			Low Permeability		
	Before	Tech	After	Before	Tech	After	Before	Tech	After	Before	Tech	After
Vapor	2	0	2	3	0	3	2	0	2	2	0	2
DNAPL	2	0	2	4	0	4						
Aqueous	2	0	2	4	2	2	3	1	2	2	0	2
Sorbed	2	0	2	4	1	3	3	1	2	2	0	2

Figure 22 - Anticipated outcome from source zone pump and treat in a middle stage Type 3 setting. Boxes in the “Tech” columns show estimated performance of remedial action based on number of OoMs of concentration reduction. “After” values equal “Before” values minus “Tech” values.

A comparison of Figure 21 and Figure 22 illustrates:

- The effectiveness of source zone pump and treat (and many other technologies) is dependent on the setting and the stage, or age, of the release.
- Care needs to be employed in discounting or strongly advocating any technology for all situations.

Favorable Attributes – In general, pump and treat systems are relatively easy to permit, design, and operate. Furthermore, capital costs are often low compared to other options. They also have the potential to serve as reliable hydraulic containment systems.

Unfavorable Attributes – Use of pump and treat systems to deplete subsurface contamination can require extended operations due to slow release of contaminant from compartments that are not directly affected by extracting water from transmissive zones. Long-term operations are commonly required, and cumulative operations and maintenance costs often become burdensome.

Excavation

Description - Excavation involves physical removal of impacted sediment and water from source zones. Options for managing excavated materials include offsite disposal at a permitted facility, on site stabilization (e.g., in a corrective action management unit), and *ex situ* treatment.

Governing Processes – Excavating equipment such as track-mounted backhoes are used to remove impacted media. Materials are often stabilized, placed in roll-off bins and subsequently transported to a permitted disposal facility. Excavations below the water table can require shoring, barriers to control groundwater (e.g., sheet pile walls), and/or dewater systems. With highly contaminated media, vapor emission may drive a need for respiratory protection for workers and measures to mitigate off-site air quality impacts.



Photo provided by Tom Sale /
Colorado State University

Figure 23 maps the anticipated effect of source excavation. The figure assumes that excavation addresses the entire source zone. It is worth noting that it has been common for excavation to miss a portion of a source. Pragmatic constraints to complete source excavation include incomplete site characterization, surface obstructions (e.g., buildings), and sediments that cannot be excavated. General insights from Figure 23 include:

- Given ideal implementation, all contamination in the source zone will be removed. Note that there are circumstances where this may not be possible.
- Contaminants stored in the plume (e.g., in low permeability zones) can sustain aqueous concentrations in the plume for extended periods of time. Plume storage will be a more significant issue in aerobic plumes with little if any ongoing degradation of contaminants in the plume.

Excavation 14 Compartment Performance Chart

Phase / Zone	Source Zone		Plume	
	Low Permeability	Transmissive	Transmissive	Low Permeability
Vapor	3-4 - Assuming that the entire source zones is removed, and properly backfilled, no contamination should remain in the source zones		0 - Extraction of aqueous phase contaminants from the transmissive zones is likely to have little effect on vapor phase contaminants	
DNAPL				
Aqueous			 1-2 - Removal of the upgradient source should yield 1 to 2 OoM improvements in downgradient water quality	0 - Depletion of contamination in the transmissive zones results in slow release of aqueous and sorbed phases in low permeability zones
Sorbed			1-2 - Depletion of the aqueous phase in transmissive zones will drive release of sorbed compounds. Note release of sorbed phase can be a slow process.	

Figure 23 – Source excavation mapped on the 14 Compartment Model for late stage Type III setting. The plume response represents conditions several years after source removal.

Niche – Excavation is typically only applicable to source zones in unconsolidated media. In general, the cost of excavation prohibits its use in plumes. The best-case scenario is that excavation occurs shortly after a release occurs (early stage), meaning that little contamination has moved into the plume (see plume Transmissive-Aqueous Figure 24). Figure 24 maps the anticipated performance of excavation in an early-stage Type III setting. Notes of caution in this analysis include the facts that: 1) It is rare that sources are removed before a plume forms and 2) Complete excavation of a source is often impractical.

Zone/ Phases	Source Zone						Plume					
	Low Permeability			Transmissive			Transmissive			Low Permeability		
	Before	Tech	After	Before	Tech	After	Before	Tech	After	Before	Tech	After
Vapor	1	4	0	3	4	0	0	0	0	0	0	0
DNAPL	1	4	0	4	4	0						
Aqueous	1	4	0	4	4	0	2	1	1	0	0	0
Sorbed	1	4	0	4	4	0	1	1	0	0	0	0

Figure 24 - Anticipated outcome from source excavation in an early stage Type III setting.

In contrast, Figure 27 maps the anticipated performance of excavation given a late-stage Type III setting. In this case, source excavation might do little to reduce the longevity of aqueous and vapor concentrations in the plume. Comparison of Figure 24 and Figure 25 points to the value of rapid response to chlorinated solvent release. Specifically, rapid response has the potential to limit the accumulation of contaminants in low permeability zones in plumes.

Zone/ Phases	Source Zone						Plume					
	Low Permeability			Transmissive			Transmissive			Low Permeability		
	Before	Tech	After	Before	Tech	After	Before	Tech	After	Before	Tech	After
Vapor	2	4	0	1	4	0	1	0	1	1	0	1
DNAPL	0	4	0	0	4	0						
Aqueous	3	4	0	2	4	0	2	1	1	3	0	3
Sorbed	3	4	0	2	4	0	2	1	1	3	0	3

Figure 25 - Anticipated outcome from source excavation in a late stage Type III setting.

Favorable Attributes – Excavation involves conventional construction equipment that is typically readily available. Given favorable conditions for excavation and practical approaches for managing excavated materials, this is often an option that is best suited to small releases. It is one of the most reliable methods for obtaining multiple OoM concentration reduction in shallow source zones.

Unfavorable Attributes – Highly contaminated soils may necessitate respiratory protection for workers and measures to control offsite exposure. Excavations in unstable soils, below the water table, and/or close to existing structures (e.g., buildings) can be difficult and/or costly. Last, the net benefit of moving contamination from one location to another (in the case of offsite land disposal) can be viewed as having marginal value.

Soil Vapor Extraction (SVE)

Description – SVE involves extraction of soil gas from the vadose zone using vacuum pumps and conventional wells or drains. The produced gases are often treated prior to being discharged into the atmosphere. Common treatment approaches include activated carbon and thermal reactors.



Courtesy of Johnson, P., R. Johnson, and M. Marley, (2000).

Formation sweep efficiencies can be enhanced by providing vent wells or drainlines to bring air into the targeted intervals. A comprehensive review of SVE is provided in U.S. EPA (1997) and COE (2002).

Variations of SVE include dual phase extraction and air sparging. Dual phase extraction involves concurrent extraction of groundwater and soil gas. Air sparging involves concurrent injection of air into the groundwater zone and recovery of soil gas. Given the limited use of dual phase extraction and air sparging for chlorinated solvent sites, these technologies are not given further consideration.

Governing Processes – SVE relies on partitioning chlorinated solvent in NAPL, aqueous, and sorbed phases (in the vadose zone) into soil gas. Slow mass transfer from any of these phases (e.g., any of the phases in a fully saturated low permeability layer in the vadose zone) can lead to an extended period of operations.

Anticipated Performance - Figure 26 maps the performance of SVE in the vadose zone. Figure 26 assumes that the source zone and vapor plume occur only in the vadose zone and, correspondingly, that there is no contamination in the groundwater zone. At many sites, however, sources and plumes occur in *both* the vadose and groundwater zones. At sites such as this, SVE would only be a partial solution as it would likely have limited effect on the groundwater zone due to slow rates of mass transfer from groundwater (diffusion limited) to soil vapor.

Soil Vapor Extraction 14 Compartment Performance Chart

Phase / Zone	Source Zone		Plume	
	Low Permeability	Transmissive	Transmissive	Low Permeability
	0-1 High water saturations in low permeability may limit extraction of vapor from low permeability zones	2-3 Vapor extraction will cause direct depletion of the vapor in transmissive zones. Effectiveness will depend on sweep efficiencies and loading from adjacent compartments.		0-1 High water saturations in low permeability may limit extraction of vapor from low permeability zones
DNAPL	0-1 Low rates of vapor flow through low permeability zones may yield very slow rates of depletion of DNAPL, aqueous, and sorbed phase from low permeability zones	2 - DNAPLs can be depleted through direct vaporization. Depletion of large bodies of DNAPL may require extended periods.		
Aqueous Sorbed		2 - Partition of dissolved and sorbed phases will sustain concentration in the vapor phase. Extended period may be required to achieve high levels of depletion.	0-1 Low rates of vapor flow through low permeability zones may yield very slow rates of depletion of phases in low permeability zones.	

Figure 26 - Source excavation mapped on the 14 compartment model for late stage Type 3 vadose zone setting . Plume conditions are considered to represent conditions years several years after source removal and near the former source.

Niche – SVE is most commonly applied in Type III settings with large depths to groundwater. Given a large vapor phase diffusion coefficient, it is not common to find DNAPL in the vadose zone. Consequently, most vadose zone releases are late-stage scenarios. Figure 27 maps the anticipated performance of SVE in a late-stage Type III setting. For the presented scenario, the primary performance limitation is addressing contaminant in low permeability zones. Slow release of contaminant from low permeability zones to the vadose zones is described in Barnes and McWhorter (2000).

Zone/ Phases	Source Zone						Plume					
	Low Permeability			Transmissive			Transmissive			Low Permeability		
	Before	Tech	After	Before	Tech	After	Before	Tech	After	Before	Tech	After
Vapor	3	1	2	2	3	0	2	3	0	2	1	1
DNAPL	1	1	0	1	2	0						
Aqueous	3	1	2	2	2	0	2	2	0	2	1	1
Sorbed	3	1	2	2	2	0	2	2	0	2	1	1

Figure 27 - Anticipated outcome from SVE in a vadose zone only for a late stage Type III setting.

Favorable Attributes – In general, SVE systems are relatively easy to permit, design, and operate. Furthermore, capital costs are generally low compared to other options.

Unfavorable Attributes – Use of SVE to deplete subsurface contamination can be a slow process. Long-term operations are commonly required and cumulative operations and maintenance costs often become burdensome.

In Situ Degradation

Today's primary suite of *in situ* degradation technologies for chlorinated solvents includes conductive heating, chemical oxidation, biological reduction, and chemical reduction.

Thermal

Description – Heat has been delivered to chlorinated solvent source zones using steam, electrical resistance heating, and conductive heating (Davis, 2008). Each approach has advantages and limitations. Today the most widely used approach is conductive heating. The following section describes conductive heating. Comprehensive information regarding the performance of thermal treatment (including conductive heating) can be found in SERDP/ESTCP reports including Johnson et al. (2010).

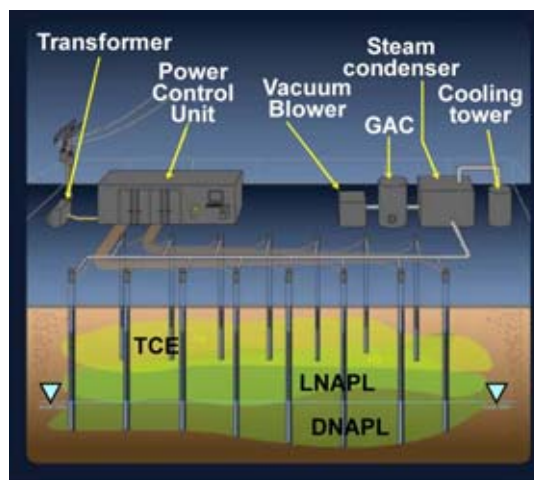


Image from ESTCP Report /
Johnson et al. (2010)

Governing Processes – Conductive heating involves placing electrical resistance heating elements through a targeted zone. Electrical current is passed through the resistors to generate heat that subsequently moves through the targeted media via conduction. Contaminants are either destroyed *in situ* via pyrolysis or recovered via vapor or liquid recovery systems. Recovered vapor and/or water are treated (e.g., thermal oxidation) prior to release. Typically, heating is continued until temperatures throughout the target are elevated to the boiling point of water, and contaminant concentrations in off gas fall to low levels. The target can be in the vadose zone, in the groundwater zone, or a combination of both. In general it is more difficult to treat the groundwater zone due to higher water content and the potential for inflow of cool groundwater during treatment.

Anticipated Performance – Respectively, Figure 28 and Figure 29 map the anticipated performance of conductive heating in the vadose zone and the groundwater zone. Both figures assume that the entire source zone is addressed. Pragmatic constraints to

addressing an entire source zone can include incomplete site characterization and surface obstructions (e.g., buildings).

Vadose Zone Conductive Heating - 14 Compartment Performance Chart


Phase / Zone	Source Zone		Plume	
	Low Permeability	Transmissive	Transmissive	Low Permeability
Vapor	3-4 - Assuming that the entire vadose source zones is addressed and heated for a sufficient period little to no contamination should remain in the source zones 		1 – Reductions in diffusive flux from the source may reduce vapor phase concentrations in the adjacent plume	0 - High water content in low permeability zones may limit release of vapor phase contaminant from low permeability zones
DNAPL				
Aqueous			1 – Reduction in pore water concentration will follow vapor phase concentrations	0 – Aqueous phase diffusive and advective transport out of low permeability zones is likely to be small
Sorbed		1- Depletion of the aqueous phase in transmissive zones will drive release of sorbed compounds. Note release of sorbed phase can be a slow process.	0 – Reduction in sorbed contaminants in the low permeability zone will follow aqueous phase concentrations in low permeability zones pore	

Figure 28 – Vadose zone conductive heating mapped on the 14 Compartment Model. Plume conditions are considered to represent conditions several years after source removal and near the former source.

Groundwater Zone Conductive Heating - 14 Compartment Performance Chart



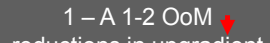
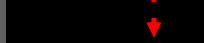
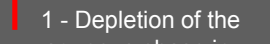
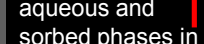
Phase / Zone	Source Zone		Plume	
	Low Permeability	Transmissive	Transmissive	Low Permeability
Vapor	2-3 - Assuming that the entire source zones is addressed and heated for a sufficient period 1 to 2 OoM have been observed in field projects (Kingston 2008). Treatment can be limited by in flow of cool groundwater. 		0 – Reductions in aqueous phase contaminants from the transmissive zones is likely to have little effect on vapor phase contaminants	
DNAPL				
Aqueous			1 – A 1-2 OoM reductions in upgradient contaminant discharge should yield 1 OoM improvements in downgradient water quality 	0 - Depletion of contamination in the transmissive zones results in slow release of aqueous and sorbed phases in low permeability zones 
Sorbed			1 - Depletion of the aqueous phase in transmissive zones will drive release of sorbed compounds. Note release of sorbed phase can be a slow process. 	

Figure 29 – Groundwater zone conductive heating mapped on the 14 Compartment Model. Plume conditions are considered to represent conditions years several years after source removal and near the former source.

Niche – Conductive heating has been employed in both unconsolidated and consolidated media. Given a relatively high implementation cost, it is typically only used in source zones. Conductive heating can perform extremely well for volatile compounds in unsaturated soils, and is also likely to be more effective with DNAPL and contaminants in low permeability zones than injection-based degradation technologies such as bioremediation and chemical oxidation. Figure 30 and Figure 31 map the anticipated performance of conductive heating on middle stage Type III setting in the vadose and groundwater zones, respectively.

Zone/ Phases	Source Zone						Plume					
	Low Permeability			Transmissive			Transmissive			Low Permeability		
	Before	Tech	After	Before	Tech	After	Before	Tech	After	Before	Tech	After
Vapor	2	3	0	3	3	0	2	1	1	2	0	2
DNAPL	2	3	0	4	4	0						
Aqueous	2	3	0	4	3	0	3	1	2	2	0	2
Sorbed	2	3	0	4	3	0	3	1	2	2	0	2

Figure 30 - Anticipated outcome from vadose zone conductive heating in a middle stage Type 3 setting.

Zone/ Phases	Source Zone						Plume					
	Low Permeability			Transmissive			Transmissive			Low Permeability		
	Before	Tech	After	Before	Tech	After	Before	Tech	After	Before	Tech	After
Vapor	2	1	1	3	2	1	2	0	2	2	0	2
DNAPL	2	1	1	4	2	2						
Aqueous	2	1	1	4	2	2	3	1	2	2	0	2
Sorbed	2	1	1	4	2	2	3	1	2	2	0	2

Figure 31 - Anticipated outcome from groundwater zone conductive heating in a middle stage Type 3 setting.

Favorable Attributes – The potential to achieve high levels of contaminant depletion including DNAPL and contaminants in low permeability zones has led to wide use of this technology.

Unfavorable Attributes – Challenging attributes include:

- The technical skill needed to implement this technology is high.
- Cost, energy use, and carbon footprint can be high.
- Incomplete heating, inflow of low-temperature groundwater, and missed portions of the source zones can lead to significant mass remaining in source zone.
- Independent of source depletion, plume concentrations can be sustained for an extended period via release of contaminants stored in the plume.
- A large number of vertical holes need to be placed through the target. Care may be needed to limit remedy-related vertical migration of DNAPL.

In Situ Chemical Reduction (ISCR)

Description – Zero valent iron (ZVI) can be used to drive reductive dechlorination of most chlorinated solvents (Gillham and O’Hannesin, 1994). Initially, ZVI was employed in permeable reactor barriers (PRBs). PRBs are covered in the following subsection on containment. ZVI has also been introduced to source zones via injection and *in situ* soil mixing. The following



Photo Courtesy of Chris Bozzini / CH2M HILL

development focuses on ZVI delivery via *in situ* soil mixing using a process referred to as ZVI-Clay (Olson et al., 2011). Concurrent with mixing, a water-based grout of clay and iron is delivered to an *in situ* mixing tool. Mixing can be achieved using larger-diameter augers, backhoe-mounted hydraulic mixing tools, and/or conventional excavation equipment. The authors are aware of nine full-scale ZVI-Clay treatments have been completed, leading to degradation of approximately 80 tons of chlorinated solvents.

Governing Processes – Corrosion of ZVI creates thermodynamic conditions that drive reductive dechlorination. The net effect is replacement of carbon-chlorine bonds with carbon-hydrogen bonds. With ZVI-Clay, the clay reduces the permeability of the treated media. One of many benefits of reduced permeability is that it extends the amount of time over which reactions can take place. After mixing, concentrations of chlorinated solvents in water and soil decay over time. Typical chlorinated solvent depletion observed after one year has been in the range of 99 to 99.99%. Slower rates of treatment may occur in areas with large amounts of DNAPL. Typical reductions in the hydraulic conductivity of the treated body are two to four OoMs. A primary result of ZVI-Clay is a significant reduction in contaminant discharge from the treated body through the combined effects of reduced concentrations and groundwater flow.

Anticipated Performance – Figure 32 maps the anticipated performance of ZVI-Clay. As with excavation and thermal treatment, the figure assumes that the entire source zone

is addressed. Pragmatic constraints to addressing an entire source zone can include incomplete site characterization and surface obstructions (e.g., buildings). Similar to excavation and thermal observation from Figure 10 include:

- Given ideal implementation, the vast majority of contamination in the treatment zone will be removed.
- Contaminants stored in the plume (e.g., in low permeability zones) can sustain aqueous concentration in the plume for extended periods of time.

Phase / Zone	Source Zone		Plume		
	Low Permeability	Transmissive	Transmissive	Low Permeability	
Vapor	2-4 - Assuming that the entire source zones is addressed and heated for a sufficient period no contamination should remain in the source zones		0 - Extraction of aqueous phase contaminants from the transmissive zones is likely to have little effect on vapor phase contaminants		
DNAPL			1-2 - Removal of the upgradient source should yield 1 to 2 OoM improvements in downgradient water quality		0 - Depletion of contamination in the transmissive zones results in slow release of aqueous and sorbed phases in low permeability zones
Aqueous					1-2 - Depletion of the aqueous phase in transmissive zones will drive release of sorbed compounds. Note release of sorbed phase can be a slow process.
Sorbed					

The diagram includes several annotations: a red arrow points from the 'Aqueous' row of the Source Zone to the 'Aqueous' row of the Plume; a red arrow points from the 'Aqueous' row of the Plume to the 'Sorbed' row of the Plume; a red arrow points from the 'Sorbed' row of the Plume to the 'Aqueous' row of the Plume; a red arrow points from the 'Vapor' row of the Plume to the 'Aqueous' row of the Plume; a red arrow points from the 'DNAPL' row of the Plume to the 'Aqueous' row of the Plume; a green circle with a red slash is positioned between the 'Aqueous' row of the Source Zone and the 'Aqueous' row of the Plume.

Figure 32 – ZVI-Clay mapped on the 14 Compartment Model. Plume conditions are considered to represent conditions years several years after source removal and near the former source.

Niche – Mixing with concurrent addition of treatment media is only feasible in soils that can readily be mixed (sand, silt, and/or clay). Treatment depths of 50 feet are generally feasible. Given a relatively high implementation cost, ZVI-Clay is typically used only in source zones. Impressively, mixing with concurrent addition of treatment media (ZVI) has extremely high performance even for zones containing DNAPL and contaminants in low permeability zones. Figure 33 maps the anticipated performance of ZVI-Clay on a middle-stage Type III setting.

Zone/ Phases	Source Zone						Plume					
	Low Permeability			Transmissive			Transmissive			Low Permeability		
	Before	Tech	After	Before	Tech	After	Before	Tech	After	Before	Tech	After
Vapor	2	3	0	3	3	0	2	0	2	2	0	2
DNAPL	2	3	0	4	3	1						
Aqueous	2	3	0	4	3	0	3	1	2	2	0	2
Sorbed	2	3	0	4	3	0	3	1	2	2	0	2

Figure 33 - Anticipated outcome from ZVI-Clay in a middle stage Type III setting.

Favorable Attributes – The technology is simple and can be implemented using readily available equipment. It has the potential to achieve levels of treatment similar to thermal, including DNAPL and contaminants in low permeability zones, at lower cost.

Unfavorable Attributes –

- Addition of water and clay reduces the compressive strength of the treated media. Post-treatment capping and/or soil stabilization may be required for select land usages.
- Applications are limited to sites that are largely free of surface or buried obstructions.

In Situ Chemical Oxidation (ISCO)

Description – Chemical oxidants, including permanganate, peroxide, activated persulfate, and ozone, have been used to drive *in situ* degradation of chlorinated solvents. Each of these oxidants has advantages and limitations. The following discussion is based on the use of permanganate as the oxidant. Permanganate was the first oxidant to be proposed (Farquhar, 1992), and typically has the advantage

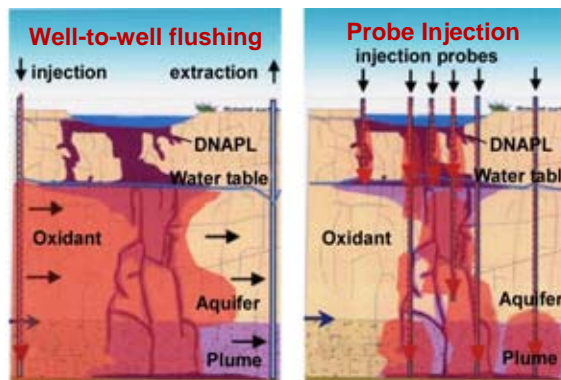


Image from ESTCP Project Report / Siegrist et al.

of persisting longest in the subsurface. A limitation of permanganate is that it is typically effective for chlorinated ethenes but not for chlorinated ethanes. Commonly, application of ISCO involves through multiple injection events. The periods between injection events are typically on the order of months to a year. Hundreds of ISCO remedies have been implemented at chlorinated solvent sites. Comprehensive information regarding ISCO can be found in SERDP/ESTCP reports including Siegrist et al. (2006) and in Brown (2010).

Governing Processes – Strong oxidants create thermodynamic conditions that favor replacement of carbon-chlorine bonds with carbon-oxygen bonds. As with all injection-based remedies, achieving effective contact between reagents and contaminants can be challenging. Constraints include:

- Displacement of dissolved phase chlorinated solvents in transmissive zones by the injected solutions
- Preferential flow of reagents through intervals of high permeability
- Potentially large stoichiometric oxidant demands of DNAPL
- Overcoming the natural oxidant demand of sediments in the targeted treatment zone
- Density-driven flow of delivered reagents
- Slow rates of reagent diffusion into low permeability zones

Post-treatment rebound of aqueous concentrations in transmissive zones, based on water samples from wells, has commonly been observed with ISCO remedies (McGuire et al., 2006). Possible explanations include release of contaminant from low permeability zones, dissolution of DNAPL, and disruption in natural attenuation processes.

Anticipated Performance – Figure 34 maps the anticipated performance of permanganate-based ISCO. The figure assumes that the entire source zone and plume are addressed.

Phase / Zone	Source Zone		Plume	
	Low Permeability	Transmissive	Transmissive	Low Permeability
Vapor	0- Depletion of contaminants in the saturated zones is likely to have little effect on vapor phase contaminants			
DNAPL	0- Slow inward diffusion of permanganate into low permeability zones and stoichiometric considerations will limit effectiveness	0-1 - DNAPL, if present in large amounts, will be difficult to deplete using chemical oxidants due to delivery and stoichiometric considerations		
Aqueous	1- Slow inward diffusion of permanganate into low permeability zones may drive partial depletion of contaminants in low permeability zones.	2 - Where mixing occurs high level of treatment can be achieved. Treatment can be limited by non-uniform delivery and releases from DNAPL and low permeability zones		
Sorbed		2- Chemical oxidants can consume natural organic carbon that sorbs chlorinated solvents. With release from sorption sites the contaminants can be depleted in the aqueous phase.	1- Slow inward diffusion of permanganate into low permeability zones may drive partial depletion of contaminants in low permeability zones.	

Figure 34 – Permanganate ISCO mapped on the 14 Compartment Model. Performance is considered to represent conditions several years after concurrent treatment of a source zone and plume.

Niche – Delivery of chemical oxidants via injection requires subsurface media with moderate to high hydraulic conductivity values ($> 10^{-4}$ cm/sec). Furthermore, it may be necessary to have injection wells on close centers (e.g., 30 feet or less). Most often chemical injection applications have been in unconsolidated alluvium as opposed to rock. The oxidant demand is an important component of any ISCO application: systems that are anaerobic or anoxic with low natural organic carbon have lower natural oxidant demands, while treatment of large DNAPL masses may be difficult due to the high chemical demand. As an example, Figure 35 maps the anticipated performance of permanganate based ISCO on a middle-stage Type III setting.

Zone/ Phases	Source Zone						Plume					
	Low Permeability			Transmissive			Transmissive			Low Permeability		
	Before	Tech	After	Before	Tech	After	Before	Tech	After	Before	Tech	After
Vapor	2	0	2	3	0	3	2	0	2	2	0	2
DNAPL	2	0	2	4	0	4						
Aqueous	2	1	1	4	1	3	3	2	1	2	1	1
Sorbed	2	1	1	4	1	3	3	2	1	2	1	1

Figure 35 - Anticipated outcome from ISCO in a middle-stage III setting.

Favorable Attributes – The technology is relatively simple and can be implemented using common equipment.

Unfavorable Attributes – Challenging attributes include:

- Post-treatment rebound and the frequent need to conduct multiple rounds of reagent delivery
- Limited contact between reactant and contaminants due to preferential flow paths
- Cost associated with oxidants and delivery limit the size of treatment
- Possible secondary water quality effects such as high sulfate with persulfate and trace metal with permanganate

In Situ Biological Treatment

Description – *In situ* biological treatment involves addition of a soluble carbon source or electron donor. Biologically mediated degradation of the carbon then depletes natural electron acceptors (e.g., oxygen, nitrate, ferric iron, and sulfate) which create conditions that favor reductive dechlorination of chlorinated ethenes. Common electron donors include vegetable oil, molasses, lactate, and whey.

In almost all instances, an electron donor is injected into the subsurface. Injection can also be coupled with ground-water extraction to draw the electron donor through the source zone. At most sites, multiple cycles of injection are employed, where typical periods between injections are on the order of one year.

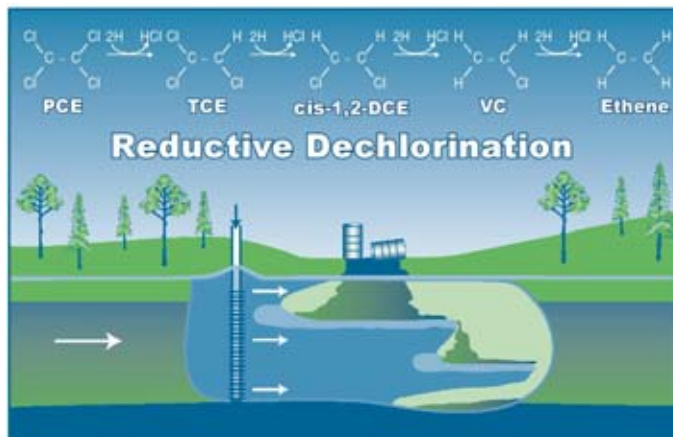


Image from ITRC 2008

Hundreds of *in situ* biological treatments have been employed at chlorinated solvent sites. Further information regarding *in situ* bioremediation for source zones can be found in SERDP/ESTCP reports, including project ER-200008 and 200438 (available at www.serdp-estcp.org) and in ITRC (2008).

Governing Processes – Uptake of electron acceptors through biological degradation of an electron donor creates thermodynamic conditions that favor reductive dechlorination of chlorinated solvents (replacement of carbon-chlorine bonds with carbon-hydrogen bonds). As with other injection-based remedies, achieving effective contact between reagents and contaminants can be challenging. Delivery-related constraints for *in situ* biological treatment include:

- Displacement of dissolved phase chlorinated solvent in transmissive zones by the injected solutions
- Preferential flow of reagents through intervals of high permeability
- Slow dissolution of DNAPL
- The potential for limited biological activity in low permeability zones

As compared to ISCO, rebound of aqueous concentrations in transmissive zones was not observed in the 20-site database described in McGuire et al., 2006. One possible explanation for less rebound with biological treatment is a greater persistence of the treatment, the buildup of endogenous biomass, and the creation of an active geochemical zone for abiotic reactions.

Anticipated Performance – Figure 36 maps the anticipated performance of *In Situ* Biological Treatment. It assumes that the source zone and plume are concurrently addressed. A primary assumption in Figure 36 is that there will be little if any stimulation

of biological activity in low permeability zones. This is a hypothesis and the topic of ongoing research. In select instances, there may be important exceptions to this position.

Phase / Zone	Source Zone		Plume	
	Low Permeability	Transmissive	Transmissive	Low Permeability
Vapor	0- Depletion of contaminants in the saturated zones is likely to have little effect on vapor phase contaminants			
DNAPL	0 - high concentration in DNAPL and the potential for limited biological activity in low permeability zone	0-1 - DNAPL, if present in large amounts, will be difficult to deplete using biological processes due to delivery and stoichiometric considerations	Not Applicable	
Aqueous	0-1 - It is anticipated that stimulation of biological activity in low permeability zones will be difficult. At best reduced concentrations in transmissive zone will accelerate release of contaminants in low permeability zones.	2 - Where mixing occurs high level of treatment can be achieved. Treatment can be limited by non-uniform delivery and releases from DNAPL and low permeability zones	0-1 - It is anticipated that stimulation of biological activity in low permeability zones will be difficult. At best reduced concentrations in transmissive zone will accelerate release of contaminants in low permeability zones.	
Sorbed		1 - The stability of natural organic carbon under reducing conditions has the potential to sustain releases for solids. Also, low solubility electron donor (e.g. vegetable oil) can sorb aqueous phase chlorinated solvents		

Figure 36 – In situ bioremediation mapped on the 14 Compartment Model. Plume conditions are considered to represent conditions years several years after treatment of a source zone and plume.

Niche – Most applications have been in unconsolidated alluvium as opposed to rock. Delivery via direct injection typically has injection points spaced at 30 feet or less, and requires soils with moderate to high hydraulic conductivity values ($> 10^{-4}$ cm/sec). Plume treatment based on electron donor addition using larger well spacing and injection/pumping methods are also used. For example, Figure 37 maps the anticipated performance of *in situ* biodegradation for source zone treatment on a middle-stage Type III setting.

Zone/ Phases	Source Zone						Plume					
	Low Permeability			Transmissive			Transmissive			Low Permeability		
	Before	Tech	After	Before	Tech	After	Before	Tech	After	Before	Tech	After
Vapor	2	0	2	3	0	3	2	0	2	2	0	2
DNAPL	2	0	2	4	0	4						
Aqueous	2	0	2	4	2	2	3	2	1	2	1	1
Sorbed	2	0	2	4	1	3	3	1	2	2	1	1

Figure 37 - Anticipated outcome from in situ biological treatment of a source zone in a middle stage Type III setting.

Favorable Attributes – The technology is relatively simple and can be implemented using common equipment. Also, implementation costs can be low relative to other options.

Unfavorable Attributes – Challenging attributes include:

- Implementation and monitoring may require long periods (e.g., many years)
- Multiple injections of electron donor may be required
- Secondary water quality issues, such as elevated levels of arsenic, heavy metals, and methane, have been identified as a potential negative outcome of *in situ* biodegradation projects.

Containment

At many sites consequential treatment of chlorinated solvents is impractical due to the size of the treatment zone, ongoing land use, finite financial resources, and/or hydrogeologic conditions. In such instances containment strategies may be the only practicable means to attain absolute objectives. The following section reviews hydraulic barriers, physical barriers, and permeable reactive barriers. Attributes common to all contaminant discharge include:

- Reduced contaminant discharge along a control boundary
- Little if any depletion of contaminants upgradient of the control boundary

Hydraulic Controls

Description – Extraction of groundwater downgradient of a source can be used to limit further contaminant discharge to a downgradient plume. Treated water is typically treated prior to discharge to a publicly owned water treatment plant or surface water body. Alternatively, treated water can be returned to the aquifer via recharge wells or infiltration wells.

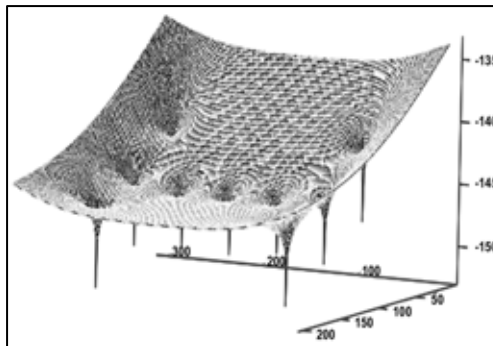


Image provided by Tom Sale
/ Colorado State University

Governing Processes – Sufficient water needs to be produced from wells or drain lines to create a hydraulic capture zone that is wide enough to capture the targeted portion of a groundwater plume. Assuming a sloping water table, the capture zones will extend from a finite length downgradient to a stagnation zone. Groundwater beyond the stagnation zone will follow the regional flow pattern. Typically, the upgradient capture zone includes the source zone.

Anticipated Performance – Figure 38 maps the anticipated performance of hydraulic containment of a source zone. This figure represents the case where all or almost all of the groundwater flowing through the source is captured by the pumping.

Hydraulic Containment (Source) 14 Compartment Performance Chart


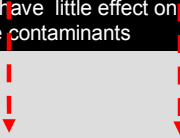
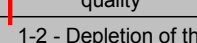
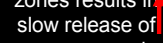
Phase / Zone	Source Zone		Plume			
	Low Permeability	Transmissive	Transmissive	Low Permeability		
Vapor	0 - Increased groundwater flow through the source zone associated with downgradient pumping will do little to reduce contaminant concentrations in any of the source zone compartments 		0 - Extraction of aqueous phase contaminants from the transmissive zones is likely to have little effect on vapor phase contaminants 			
DNAPL						
Aqueous			1-2 - Removal of the upgradient source should yield 1 to 2 OoM improvements in downgradient water quality 		0 - Depletion of contamination in the transmissive zones results in slow release of aqueous and sorbed phases in low permeability zones 	
Sorbed			1-2 - Depletion of the aqueous phase in transmissive zones will drive release of sorbed compounds. Note release of sorbed phase can be a slow process.			

Figure 38 – Hydraulic containment of a source zone mapped on the 14 Compartment Model. Plume conditions are considered to represent conditions years several years after implementation of hydraulic control.

Niche – Hydraulic containment can be implemented in almost any hydrogeologic setting. It is commonly used in bedrock settings due to the limited viability of other treatment options. Figure 39 maps the anticipated performance of hydraulic containment in a middle-stage Type III setting. Notes of caution in this analysis include:

- It is not always easy to fully capture a plume
- Releases of contaminants stored in the plume, and/or slow rates of groundwater flow in stagnant zones, may lead to persistent concentrations in the down-gradient groundwater plume.

Zone/ Phases	Source Zone						Plume					
	Low Permeability			Transmissive			Transmissive			Low Permeability		
	Before	Tech	After	Before	Tech	After	Before	Tech	After	Before	Tech	After
Vapor	2	0	2	3	0	3	2	0	2	2	0	2
DNAPL	2	0	2	4	0	4						
Aqueous	2	0	2	4	0	4	3	2	1	2	0	2
Sorbed	2	0	2	4	0	4	3	2	1	2	0	2

Figure 39 - Anticipated outcome from physical containment of a source zones of a middle stage Type 3 setting.

Favorable Attributes – The technology is relatively simple to permit, design, implement and operate. Initial capital costs can be low relative to other options. Often, this is the only practical option for challenging sites such as those with contamination in deep bedrock settings.

Unfavorable Attributes – The primary challenge is the common need for long term operations and, correspondingly, high operations and maintenance costs.

Physical Barriers

Description – Low permeability barriers such as bentonite slurry walls or sheet piling can be placed at the downgradient edges of source zones to limit further contaminant discharge to plumes. To control mounding of water on the upgradient side of barriers, and/or flow around the ends of the barriers, physical barriers often fully surround source zones. Furthermore,



Image provided by Chuck Newell / GSI Environmental Inc.

low flow pumping inside barrier walls can be employed to diminish releases via advection and/or diffusion. This development assumes that water levels inside the physical barrier

are managed in such a way that adverse outward flow from the containment doesn't occur.

Governing Processes – Physical barriers reduce mass discharge from source zones by diverting groundwater flow around the source. In theory, treatment of contaminants inside physical barriers is limited, although some researchers have observed that the elimination of fresh groundwater flow through chlorinated solvent source zones can reduce the negative impact of competing electron acceptors such as oxygen and sulfate.

Anticipated Performance – Figure 40 maps the anticipated performance of a physical barrier surrounding a source zone. Key assumptions include:

- The physical barrier encloses the vast majority of the source zone.
- Water levels inside the barrier are managed such that adverse outward flow of groundwater doesn't occur.
- The physical barrier doesn't have any major flaws.

Note that the 14 Compartment Model of physical containment (Figure 46) is identical to that of hydraulic containment (Figure 38).

Physical Containment (Source) 14 Compartment Performance Chart



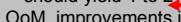


Phase / Zone	Source Zone		Plume			
	Low Permeability	Transmissive	Transmissive	Low Permeability		
Vapor	0 - Increased groundwater flow through the source zone associated with downgradient pumping will do little to reduce contaminant concentrations in any of the source zone compartments 		0 - Extraction of aqueous phase contaminants from the transmissive zones is likely to have little effect on vapor phase contaminants 			
DNAPL						
Aqueous			1-2 - Removal of the upgradient source should yield 1 to 2 OoM improvements in downgradient water quality 		0 - Depletion of contamination in the transmissive zones results in slow release of aqueous and sorbed phases 	
Sorbed			1-2 - Depletion of the aqueous phase in transmissive zones will drive release of sorbed compounds. Note release of sorbed phase can be a slow process. 			

Figure 40 – Physical containment of a source zone mapped on the 14 Compartment model. Plume conditions are considered to represent conditions years several years after containment.

Niche – Physical barriers are comprised of vertical barriers typically installed in alluvium or soft bedrock that can easily be excavated (slurry walls) or penetrated by direct push systems (sheet pile walls). At many sites, a low-permeability cap is built over the enclosed area, and a low-volume pump-and-treat system is installed to ensure an inward hydraulic gradient. Costs for constructing vertical barriers using slurry wall technology is very low for sites with good access, unconsolidated soils, and construction depths less than 50 feet. Deeper construction depths are also possible, but tend to be significantly more expensive. Figure 41 maps the anticipated performance of physical containment in a middle-stage Type III setting. Notes of caution with this analysis include:

- Past experience has shown that it is easy to miss a portion of a source zone, resulting in source materials outside the vertical barrier.
- Releases of contaminants stored in the downgradient plume and/or slow rates of groundwater flow in stagnant zones may lead to persistent concentrations in groundwater and vapor plume.

Zone/ Phases	Source Zone						Plume					
	Low Permeability			Transmissive			Transmissive			Low Permeability		
	Before	Tech	After	Before	Tech	After	Before	Tech	After	Before	Tech	After
Vapor	2	0	2	3	0	3	2	0	2	2	0	2
DNAPL	2	0	2	4	0	4						
Aqueous	2	0	2	4	0	4	3	2	1	2	0	2
Sorbed	2	0	2	4	0	4	3	2	1	2	0	2

Figure 41 - Anticipated outcome from physical containment of a source zones in a middle stage Type 3 setting.

Favorable Attributes – The technology is relatively simple to permit, design, implement and operate. For large sites physical containment often has low capital cost when compared to in-situ source treatment options. Also groundwater treatment costs can be minimized by including hydraulic barriers.

Unfavorable Attributes – The primary challenge is the common need for long-term maintenance and monitoring.

Permeable Reactive Barriers (PRBs)

Description – Granular zero valent iron (ZVI) and other permeable reactive media have been placed through groundwater plumes to form reactive barriers for chlorinated solvents. Reactions in PRBs typically leads to multiple order of magnitude (OoM) reductions in concentrations immediately downgradient of the barrier.

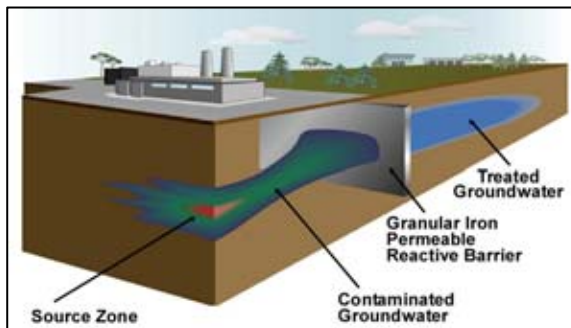


Image Courtesy of EnviroMetal Technologies Inc.

Correspondingly, multiple OoM reductions in the total mass discharge of chlorinated solvents to downgradient plumes can be achieved. The most common reactive media has been ZVI, and therefore the example application of the 14 Compartment Model is based on experiences with ZVI PRBs. Emerging and experimental alternatives to ZVI PRBs, respectively, include organic mulch (AFCEE, 2008) and electrolytic PRBs (Sale et al., 2009). Unfortunately, as with any technology that reduces contaminant discharge along a plane, releases of contaminants stored in downgradient portions of the plume can sustain groundwater plume concentrations for extended periods.

General approaches for installation of ZVI PRBs include trenching and jetting. Trenching based placement can be achieved using conventional shoring, hydraulic shoring (polymers), and continuous trenching equipment to depth as great as 50 feet. Emplacement of ZVI via jetting is more common for deep (>50 feet) foot installation. Comprehensive information regarding ZVI PRBs can be found in Gavaskar (2000), Roberts (2002), and Gavaskar (2002).

Governing Processes – Granular ZVI creates reducing conditions that drives reductive dechlorination of chlorinated ethenes. This leads to replacement of carbon-chlorine bonds with carbon-hydrogen bonds. Impacted groundwater is driven through PRBs via natural hydraulic gradients. The design thickness of a ZVI PRB is dependent on groundwater flow rates, reaction kinetics in the barrier, influent concentrations, and target effluent concentrations. Over many years (greater than 10 years), secondary inorganic precipitates and passivation of reaction sites on the iron can lead to reduced levels of treatment in ZVI PRBs.

Anticipated Performance – Figure 42 maps the anticipated performance of a ZVI PRB located at the downgradient edge of a source zone. Key assumptions include:

- The PRB intercepts the majority of the targeted plume emanating from the source
- The barrier doesn't have any major flaws
- Flow is largely normal to the plane of the PRB

An interesting footnote is that the 14 Compartment Model for applying an iron PRB is identical to that of physical containment and hydraulic containment. One key difference between PRBs and physical and hydraulic containment is that the water will flow into the plume through the source zone, and not around the source zone. Therefore, there are no stagnant zones immediately downgradient of the containment zone and clean water can slowly remove contaminants from within the plume.

ZVI PRB 14 Compartment Performance Chart

Phase / Zone	Source Zone		Plume	
	Low Permeability	Transmissive	Transmissive	Low Permeability
Vapor	0 - PRBs have no effect on upgradient contaminant concentrations.		0 - Depletion of aqueous phase contaminants from the transmissive zones is likely to have little effect on vapor phase contaminants	
DNAPL				
Aqueous			1-2 - Removal of the upgradient source should yield 1 to 2 OoM improvements in downgradient water quality	0 - Depletion of contamination in the transmissive zones results in slow release of aqueous and sorbed phases in low permeability zones
Sorbed			1-2 - Depletion of the aqueous phase in transmissive zones will drive release of sorbed compounds. Note release of sorbed phase can be a slow process.	

Figure 42 – ZVI PRB containment of a source zone mapped on the 14 Compartment Model. Plume conditions are considered to represent conditions several years after emplacement of the PRB.

Niche – ZVI PRBs are typically installed in unconsolidated soils that can easily be excavated (trench installations) or penetrated by direct push systems (jetting installations) to depths of 50 feet or less. Deeper installation depths are possible but tend to be significantly more expensive. Situations where large vertical gradients exist through the interval in which PRB would be installed can create unfavorable groundwater flow

patterns. Figure 43 maps the anticipated performance of a ZVI PRB immediately downgradient of a source zone in a middle-stage Type III setting. A note of caution is that even with relatively clean water exiting the PRB and flushing the downgradient plume, releases of contaminants stored in the downgradient plume may lead to persistent concentrations in groundwater.

Zone/ Phases	Source Zone						Plume					
	Low Permeability			Transmissive			Transmissive			Low Permeability		
	Before	Tech	After	Before	Tech	After	Before	Tech	After	Before	Tech	After
Vapor	2	0	2	3	0	3	2	0	2	2	0	2
DNAPL	2	0	2	4	0	4						
Aqueous	2	0	2	4	0	4	3	2	1	2	0	2
Sorbed	2	0	2	4	0	4	3	2	1	2	0	2

Figure 43 - Anticipated outcome from a PRB installed immediately downgradient of a source zone in a middle stage Type 3 setting.

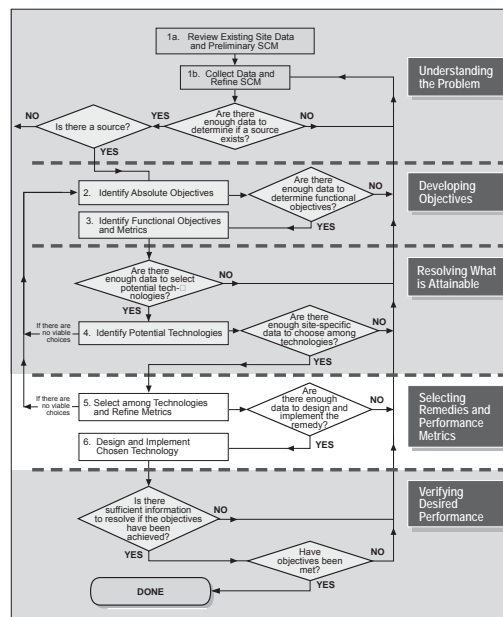
Favorable Attributes – The technology is relatively simple to permit, design, implement and operate. In general, life cycle operations and maintenance costs are low relative to hydraulic containment.

Unfavorable Attributes – The primary challenge is the initial capital cost associated with installation. Based on current information, many PRBs may need replacement or reactivation within a 10 to 30 year time period after construction.

Section 5 - Developing Packages of Remedial Measure

Last, the topic of developing comprehensive solutions for chlorinated solvent releases is addressed. Per NRC (2005), this last step builds on:

- A holistic understanding of the nature of the problem (Section 2)
- Objectives that are beneficial, attainable, verifiable, and consistent with the needs of all parties involved (Section 3)
- A site-specific understanding of what can be achieved using proven technologies (Section 4)



The process of developing packages of remedial measure is advanced through three examples. The examples were inspired by three real sites where early elements of the 14 Compartment Model were used to evaluate remedial options. Attributes of each of the sites have been intentionally modified such that none of the examples are actual sites. Nevertheless, the authors wish to recognize the significant contributions of early adopters of the 14 Compartment Model in developing the steps and graphical formats presented herein. The vision of this section is that readers can follow the steps outlined or that they may have a site that is similar to one of the examples. For each example the following are developed:

- A conceptual model that includes a 14 Compartment Model characterization of conditions at each site.
- A set of functional objectives that are used as a basis for screening remedial actions.
- An iterative development of a package of remedial measures including anticipated outcomes in terms of contaminant distribution and attainment of functional goals.

It is worth noting that development of each of the examples leads to novel ways of applying the 14 Compartment Model. We encourage readers to consider what we have done and recognize the opportunity to adapt our methods to their own needs.

Example 1 – A Large Instantaneous Release of PCE DNAPL

Site Conceptual Model

Background - Example 1 involves a large industrial facility where piping on a storage tank failed. This caused a rapid release of approximately 10,000 gallons of perchloroethene (PCE). The PCE release occurred into a thick, highly heterogeneous alluvial fan deposit containing interbeds of moderately to poorly sorted silt, fine sand, and coarse sand. Over a period of twenty years, a plume extended from the release area, or source zone, downgradient across the industrial property and ultimately into an adjacent residential neighborhood.

Figure 44 provides plan-view and cross-sectional representations of the site. For real sites, data can be overlain on plan-view maps and cross-sections to develop similar representation. The plume length is approximately 1 mile. The depth to top of the water table is a few tens of feet below ground surface (bgs). The depth to the base of PCE contamination is on the order of 40-60 feet bgs. The plume is aerobic and the absence of PCE degradation products suggests that there is little if any natural biological degradation of PCE occurring. The apparent transport velocity in the plume is 1 mile in twenty years or 260 feet/year. The apparent attenuation of aqueous phase concentrations with distance is attributed to the combined effects of sorption in transmissive zones and storage of contaminant in low permeability zones. The idea of ongoing contaminant storage in low permeability zones is stylistically shown by low permeability interbeds (lenses with dashes) that have higher concentrations at their margins than in their interiors.

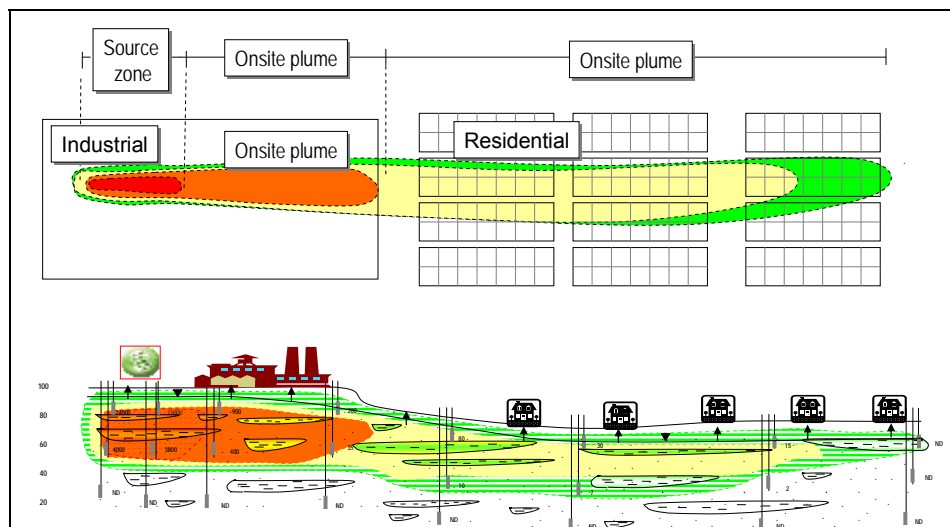


Figure 44 – Plan-view and cross-sectional representation of Example Site 1.

Note that Figure 44 splits the release into a source zone, an onsite plume, and an offsite plume. The subdivision of the plume into onsite and offsite elements is necessitated by a number of factors including different onsite and offsite:

- Exposure scenarios
- Access constraints
- Plume concentrations
- Objectives

Mapping Contaminant Distribution and Fluxes - Figure 45 employs a 14 Compartment Model OoM depiction of the contaminant distribution and contaminant fluxes. Per the terminology introduced in Section 2, the site is a middle-stage Type III site. Note that following the development in Figure 44, the 14 compartment representation in Figure 45 has been modified (relative to presentations in Sections 1 and 3) to include separate sets of compartments for the onsite and offsite plumes. The concentration estimates in Figure 45 were developed by first looking at available water quality and soil gas data. This information was used to inform the aqueous and vapor phase concentrations in transmissive zones. The remaining compartments were filled in based on anticipated partitioning between phases and transmissive and low permeability zones per the processes described in Section 2. Unfortunately, as has been typical for many sites historically, no data were available from low permeability zones. For sites where critical information is missing, efforts should be made to collect the information needed to make fully informed decisions. As a footnote, development of 14 Compartment Models can help inform decisions regarding collection of additional data. Last, Figure 45 also shows

the critical points where human exposures seem most likely to occur (offsite indoor air - house icon and groundwater - well icon). As such, the 14 Compartment Model is also used to develop a conceptual model for exposure pathways.

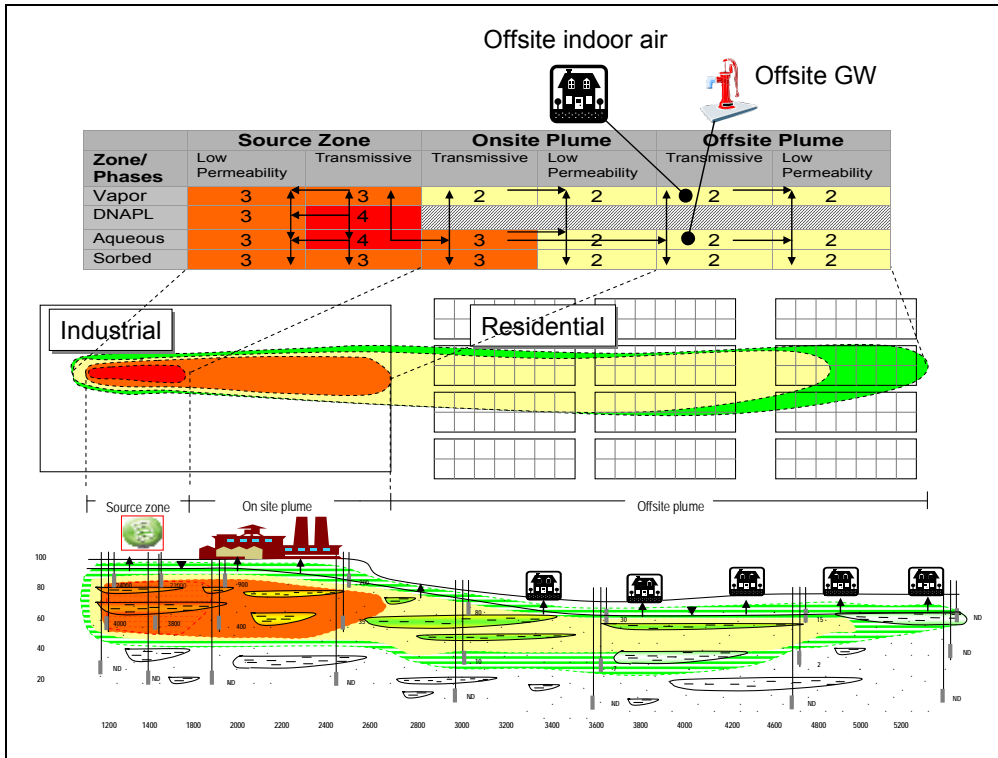


Figure 45 – Plan-view and cross-sectional representation with 14-compartment mapping of Example Site 1.

Objectives

The next step in advancing Example 1 is to develop a set of absolute and functional objectives for the site. Key drivers for stakeholders are:

- Locally, home owners in the residential area are concerned about potential health effects, potential impacts to property values, and undue disruptions in the neighborhood.
- Regionally, the community is committed to a clean environment while wanting to preserve jobs.
- The facility owners are committed to immediately addressing any complete exposure pathways and meeting all other obligations within the constraints of:
 - A preference for actions that have consequential benefits
 - Working within the bounds of what is economically feasible
 - A preference for solutions with low operations and maintenance requirements.

- Regulators wish to support the interests of the community, provide technical support to all parties, and pursue compliance with applicable rules and regulations.

Building on the discussion of absolute objectives presented in Section 3, our hypothetical (envisioned mutual consent) absolute objectives are:

- Protection of human health and the environment
- Addressing adverse community impacts
- Minimization of the burden of past practices on future generations
- Conservation of natural resources

Our hypothetical functional objectives are presented in the first column of Table 4. Additional columns to the right of the functional objectives provide a basis for qualitative ranking of how well a select action or set of actions meets the desired result in the near term (a few years) or long term (a decade or more). Inclusive to the option is the “status quo.” For this example, the status quo includes no active uses of groundwater, and vapor mitigation system on homes with potentially unacceptable indoor air contamination. The adjacent image provides an OoM rating system for attainment of functional objectives. The OoM attainment rating system is applied for the status quo in Table 4. Pragmatically, any new set of actions should result in a consequential improvement over the status quo.

Advancement of a Package of Remedial Measures

Advancement of a package of remedial measures is envisioned as an iterative process in which options are proposed, performance is anticipated, and complementary measures are added to address limitations. Our vision is that all parties with relevant interests should participate in roles that are appropriate for their interests and abilities. Our first step in this process is resolving a “first cut” set of actions that are given and, conversely, actions that are unlikely. For this example elements that are given and unlikely elements include:

- Given
 - Land use restrictions that preclude future use of groundwater in the impacted area for the foreseeable future.
 - Maintenance of vapor mitigation on all homes where a potential for adverse site related impacts exists.
 - Long-term monitoring to verify the protectiveness of the site remedy.

- Unlikely
 - Measures that would preclude reasonable continuous habitation of the homes in impacted areas.
 - Measures that would cause the industrial facility to close.

Table 4 – Functional objectives and status quo rating for Example Site 1

Term in which the result is anticipated	Status Quo	
	Short	Long
Risk		
Mitigate adverse human exposure via soil gas given current and reasonable future use	Yellow	Yellow
Mitigate adverse human exposure via groundwater given current and reasonable future use	Yellow	Yellow
Mitigate adverse worker-related exposures via soil, groundwater, and/or soil vapor	Yellow	Yellow
Avoid actions that have the potential to increase risk	Yellow	Yellow
Extent		
Prevent expansion of plumes	Grey	Grey
Reduce the extent of plumes	Grey	Grey
Longevity		
Reduce the period in which persistent releases to groundwater occur.	Grey	Grey
Reduce the period in which releases to soil gas occur.	Grey	Grey
Regulatory		
Comply with local, state, and federal regulations	Grey	Grey
Community		
Avoid undue interruptions to community	Green	Green
Land use		
Restore beneficial use of impacted lands	Grey	Grey
Economic		
Select actions that have a practical near-term capital cost and minimal life cycle cost	Yellow	Yellow
Sustainability		
Select measures that have a net positive environmental benefit	Grey	Grey
Avoid undue remedy-related interruptions to communities, government, and industry activities	Green	Green
Resource Conservation		
Limit future degradation of natural resources	Grey	Grey
Restore impacted groundwater to standards needed for beneficial use	Grey	Grey
Implementations		
Select remedies that are practical to install	Green	Green

For our hypothetical example we assume that the interested parties propose two divergent options of:

- **Source depletion** via *in situ* conductive heating
- **Source containment** via a bentonite slurry wall and low flow hydraulic containment

Figure 46 and Figure 47 anticipate the outcome of the above actions. The performance is based on the conditions identified in Figure 45 and the maps of technology performance presented in Section 4. One variation from the Section 4 input is the anticipated result that an OoM improvement in aqueous concentrations in transmissive zones in the plume will yield an OoM improvement in vapor concentrations in transmissive zones in the plume. This points out the fact that the anticipated performances for technologies described in Section 4 are guides, not fixed results.

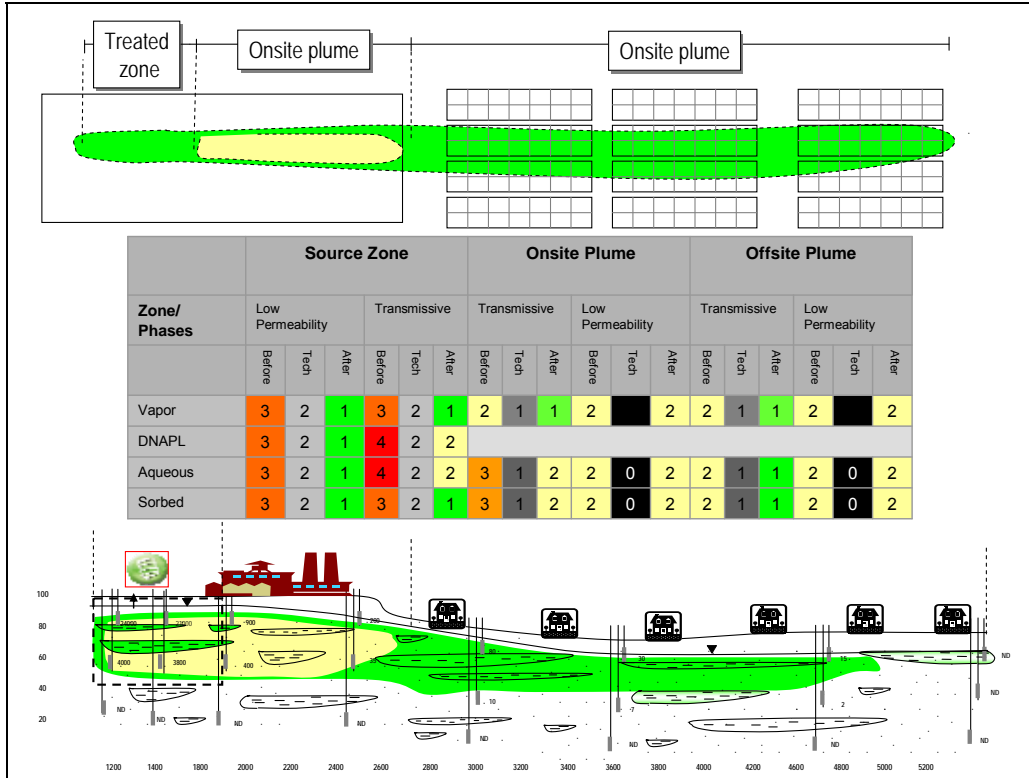


Figure 46 – Near-term (~5 years) effect of source depletion via *in situ* conductive heating

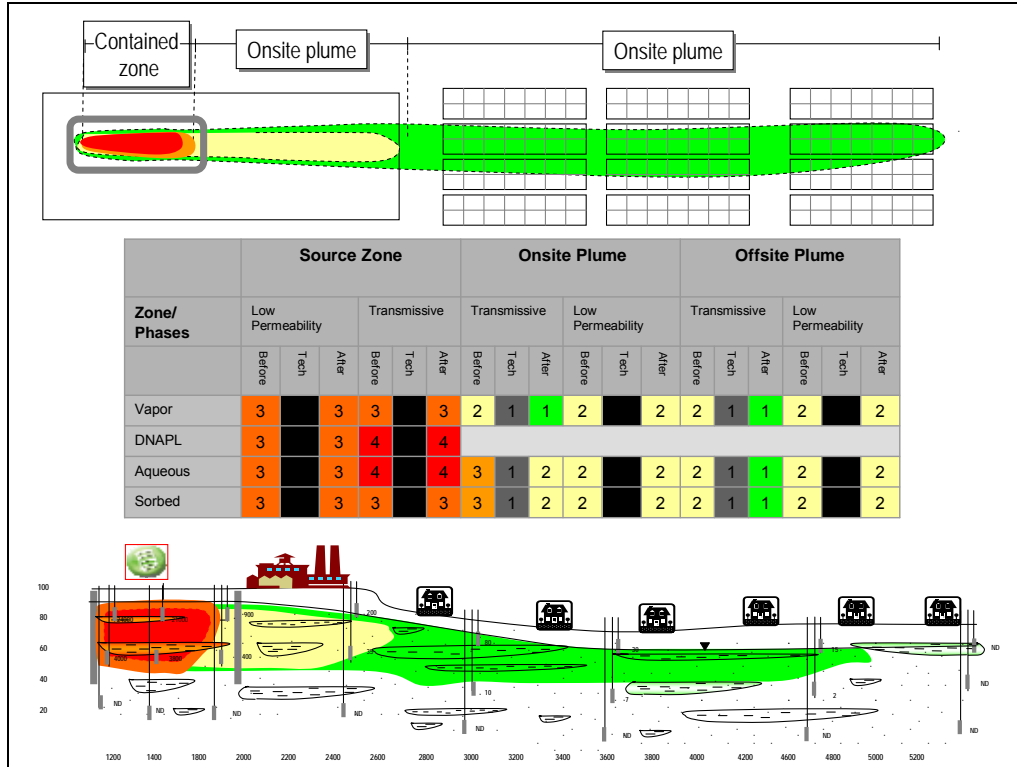


Figure 47 – Near-term (~5 years) effect of source containment via a bentonite slurry wall and low flow hydraulic containment

From a performance perspective, the primary difference between the two options is that thermal treatment depletes the source and while containment has little effect on contaminants in the source zone. From an OoM perspective, both options have similar results in the onsite and offsite plumes. Further insights regarding the merits of the options are provided in Table 5.

Per Table 5, other differences between the options are a higher capital cost and a greater disruption of site activities with the thermal options. Conversely, containment has a higher life cycle cost due to a need for long-term operation and maintenance primarily associated with hydraulic control. A limitation common to both actions is slow and only partial improvement in aqueous and vapor concentrations in the offsite plume.

Table 5 – Example 1 - Analysis of the status quo, thermal treatment of the source and containment of the source

	Status Quo		Thermal		Containment	
	Short	Long	Short	Long	Short	Long
Term in which the result is anticipated						
Risk						
Mitigate adverse human exposure via soil gas given current and reasonable future use	Yellow	Yellow	Yellow	Green	Yellow	Green
Mitigate adverse human exposure via groundwater given current and reasonable future use	Yellow	Yellow	Yellow	Green	Yellow	Green
Mitigate adverse worker-related exposures via soil, groundwater, and/or soil vapor	Yellow	Yellow	Yellow	Green	Yellow	Green
Avoid actions that have the potential to increase risk	Yellow	Yellow	Yellow	Green	Yellow	Green
Extent						
Prevent expansion of plumes	Grey	Grey	Grey	Yellow	Grey	Yellow
Reduce the extent of plumes	Grey	Grey	Grey	Yellow	Grey	Yellow
Longevity						
Reduce the period in which persistent releases to groundwater occur	Grey	Grey	Grey	Yellow	Grey	Yellow
Reduce the period in which releases to soils gas occur	Grey	Grey	Grey	Yellow	Grey	Yellow
Regulatory						
Comply with local, state, and federal regulations	Grey	Grey	Grey	Grey	Grey	Grey
Community						
Avoid undue interruptions to community	Green	Green	Green	Green	Green	Green
Land use						
Restore beneficial use of impacted lands	Grey	Grey	Grey	Yellow	Grey	Yellow
Economic						
Select actions that have a practical near-term capital cost and minimal life cycle cost	Yellow	Yellow	Red	Green	Green	Red
Sustainability						
Select measures that have a net positive environmental benefit	Grey	Grey	Grey	Yellow	Yellow	Yellow
Avoid undue remedy-related interruptions to communities, government, and industry activities	Green	Green	Yellow	Yellow	Green	Green
Resource Conservation						
Limit future degradation of natural resources	Grey	Grey	Yellow	Yellow	Yellow	Yellow
Restore impacted groundwater to standards needed for beneficial use	Grey	Grey	Grey	Grey	Grey	Grey
Implementations						
Select remedies that are practical to install	Green	Green	Yellow	Yellow	Green	Green

Building on the Table 5 analysis, the following modifications to the thermal and containment options are proposed:

- For both options, an iron permeable reactive barrier (PRB) will be added at the downgradient edge of the onsite plume. This will reduce the time needed to see improvements in aqueous and vapor phase concentrations in the offsite (residential) plume.

- For containment, an electron donor (e.g., emulsified vegetable oil) will be injected inside the bentonite slurry wall. Biological treatment is anticipated to eliminate the need for hydraulic controls inside the containment zone and, over the long term, will achieve depletion of contaminants in the source zone similar to that of the thermal treatment.

Given these additions, the performance of both options from an OoM perspective is similar.

Figure 48 anticipates the outcome of enhanced options, referred to as containment plus and thermal plus. Last, Table 6 compares the status quo, thermal plus, and containment plus. We will assume (given the two options' similar treatment outcomes) that containment plus was selected based on its lower cost and greater compatibility with ongoing industrial land use. This is where we end this example. Nevertheless, it could be carried further. For instance, active treatment could be added for the offsite plume. While active treatment in the offsite plume could yield further improvements in offsite water and soil gas quality, it might come with unacceptable disruptions to residences. Another path for the analysis would be to revisit the functional objectives. As an example, allowance for attainment of the objective over a longer period of time might be the best way to achieve more complete attainment of the function objectives. As can be seen by comparing short- and long-term results, the outcome from actions can improve with time.

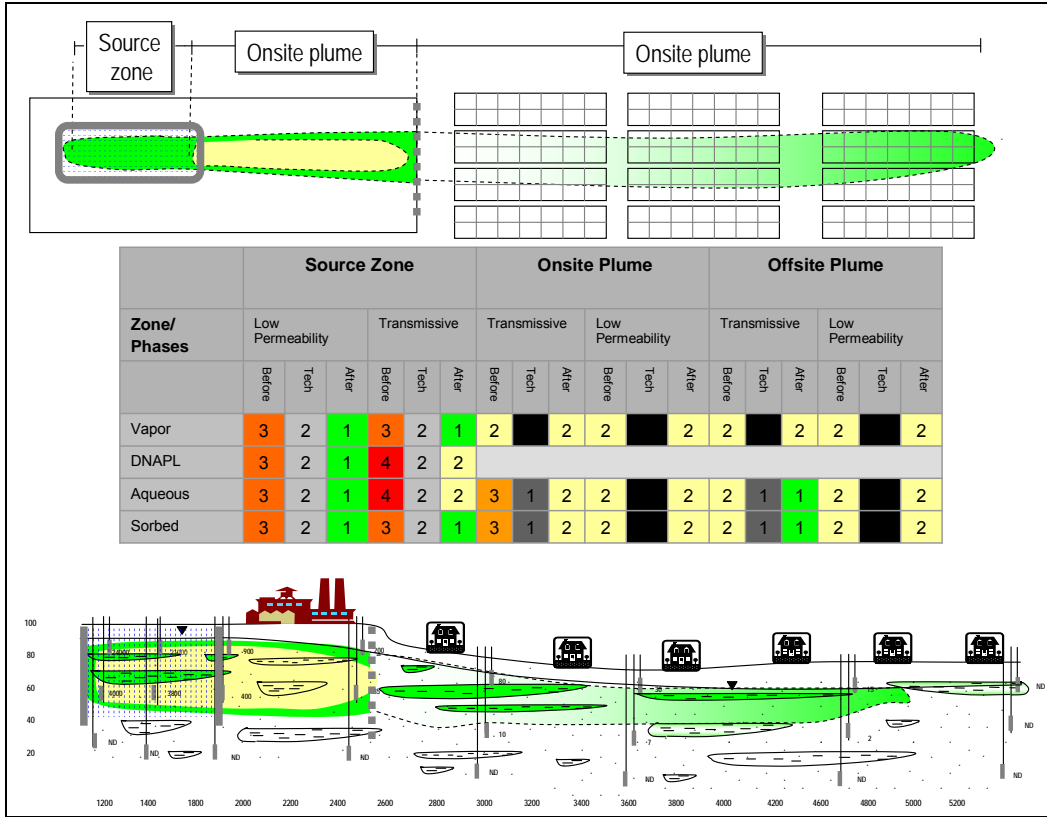


Figure 48 – Near-term (~5 years) effect of source containment via a bentonite slurry wall, PRB, and addition of an electron acceptor inside the slurry wall.

Table 6 – Example 1 - Analysis of the status quo, thermal plus, and containment plus.

	Status Quo		Thermal Plus		Containment Plus	
	Short	Long	Short	Long	Short	Long
Term in which the result is anticipated						
Risk						
Mitigate adverse human exposure via soil gas given current and reasonable future use	Yellow	Yellow	Yellow	Green	Yellow	Green
Mitigate adverse human exposure via groundwater given current and reasonable future use	Yellow	Yellow	Yellow	Green	Yellow	Green
Mitigate adverse worker-related exposures via soil, groundwater, and/or soil vapor	Yellow	Yellow	Yellow	Green	Yellow	Green
Avoid actions that have the potential to increase risk	Yellow	Yellow	Yellow	Green	Yellow	Green
Extent						
Prevent expansion of plumes	Grey	Grey	Yellow	Green	Yellow	Green
Reduce the extent of plumes	Grey	Grey	Yellow	Green	Yellow	Green
Longevity						
Reduce the period in which persistent releases to groundwater occur	Grey	Grey	Yellow	Green	Yellow	Green
Reduce the period in which releases to soil gas occur	Grey	Grey	Yellow	Green	Yellow	Green
Regulatory						
Comply with local, state, and federal regulations	Grey	Grey	Grey	Yellow	Grey	Yellow
Community						
Avoid undue interruptions to community	Green	Green	Green	Green	Green	Green
Land use						
Restore beneficial use of impacted lands	Grey	Grey	Yellow	Green	Yellow	Green
Economic						
Select actions that have a practical near-term capital cost and minimal life cycle cost	Yellow	Yellow	Red	Green	Green	Green
Sustainability						
Select measures that have a net positive environmental benefit	Grey	Grey	Grey	Yellow	Yellow	Yellow
Avoid undue remedy-related interruptions to communities, government, and industry activities	Green	Green	Yellow	Yellow	Green	Green
Resource Conservation						
Limit future degradation of natural resources	Grey	Grey	Yellow	Green	Yellow	Green
Restore impacted groundwater to standards needed for beneficial use	Grey	Grey	Grey	Yellow	Grey	Yellow
Implementations						
Select remedies that are practical to install	Green	Green	Yellow	Yellow	Green	Green

Summary –

In this example a package of remedial measures was developed through a collaborative-iterative process. Outcomes of the proposed actions were anticipated using the 14 Compartment Model and the maps of technology performance introduced in Section 4. A set of actions is advanced that provides consequential improvements over the status quo. At the same time, the solution leaves contaminants in places that will only be addressed by presumably slow natural attenuation processes. In the end, accepting a solution of this nature would be a matter of valuing what can pragmatically be achieved while planning to manage what remains.

Example 2 – A Small Release of TCE after 10 years of Hydraulic Containment

Site Conceptual Model

Background - Example 2 involves a 1950s-60s era munitions manufacturing facility where TCE was used for maintenance of munitions assembly systems and final cleaning of munitions. Process wash waters were conveyed via sewers to a pond with no discharge points. Influent flows to the pond were accommodated by evaporation and seepage losses. Seepage losses were on the order of 100s of thousand of gallon per day. Given the large volume of water and limited usages of TCE at the site, TCE released from the ponds occurred primarily in an aqueous phase. As such, there were no consequential DNAPL releases at the site, and the site does not have a source zone. A source zone is defined (per NRC, 2005) as a subsurface body in which DNAPL was released. The absence of TCE DNAPL is also consistent with the relatively high aqueous solubility of TCE (0.1%).

However, water released from the pond did contain tens of mg/L of TCE in the dissolved phase. As shown in **Figure 49**, the resultant plume extends for approximately one mile downgradient to a surface water body. The surface water body is the local discharge point for groundwater. A large part of the depth and width of the downgradient plume is attributed to the hydraulic drive created by recharge coming from the pond. Furthermore, rapid movement of the plume from the pond to the surface water body is attributed to the hydraulic gradients created by the mounding of groundwater beneath the pond. Current

rates of groundwater flow, under the natural gradient, are on the order of 100 feet per year.

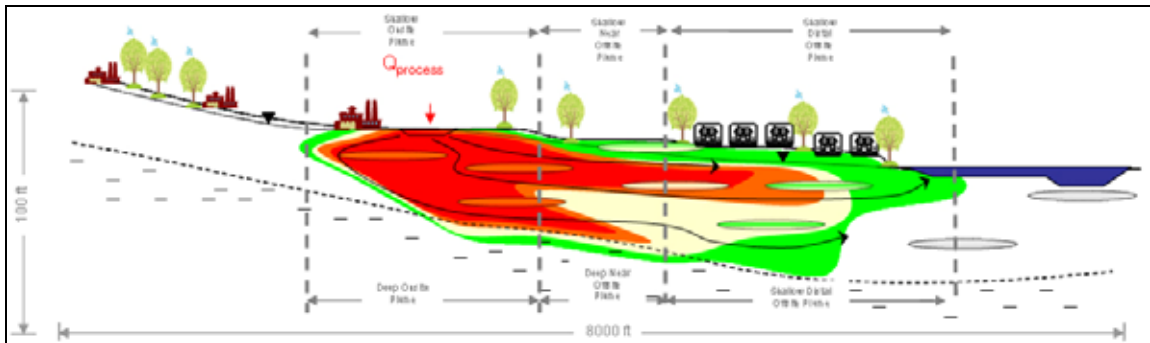


Figure 49 - Site setting and mature plumes prior to implementation of site remedies.

Geologically, the subsurface includes heterogeneous glacial outwash containing transmissive sands with interbeds of low permeability silt (0 to 40 ft bgs). Low permeability lenses in the transmissive sands are depicted stylistically as elliptical lenses with either inward or outward concentration gradients. Observed low oxidation-reduction potential (ORP) and the presence of TCE degradation products suggests that TCE is being reductively degraded, albeit slowly, via natural biological processes.

In 1970, the site operations that created the TCE plume ended. In 2000, a groundwater hydraulic control barrier was installed. Since 2000 groundwater has been produced using a line of recovery wells located downgradient of the pond. Produced water is treated via air stripping with no off gas treatment. Treated water is returned to the aquifer via a shallow onsite recharge ponds. Current conditions, including the distribution of contamination after ten years of hydraulic control, are depicted in **Figure 50**.

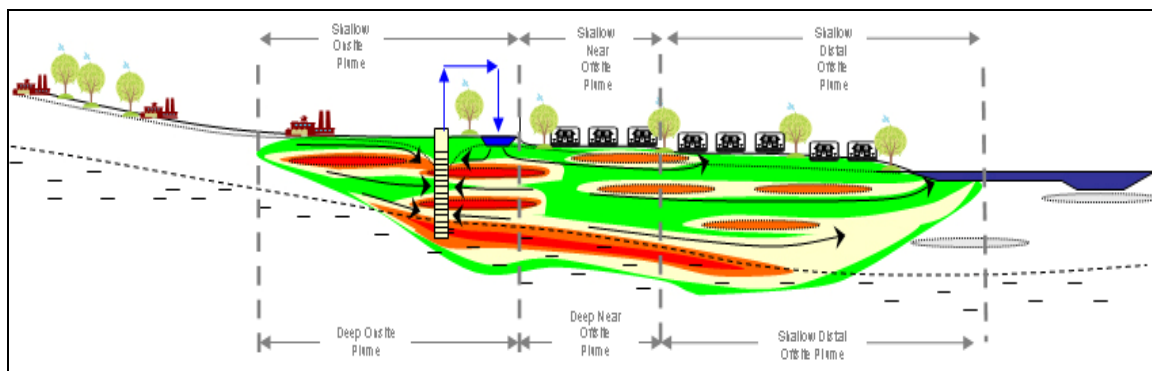


Figure 50 - Site setting and contaminant distribution 10 years after implementation of hydraulic control at the property boundary.

Figure 49 and **Figure 50** divide the release into shallow and deep - onsite, near offsite, and distal offsite plumes. The subdivisions are necessitated by a number of factors including different:

- Exposure scenarios,
- Access constraints,
- Plume concentrations,
- Applicable technologies, and
- Objectives.

Offsite concerns exist with indoor air and groundwater. All homeowners have been offered no-cost vapor mitigation systems. Many, but not all, of the homeowners in affected areas have accepted the offer. All homes are provided water via a fully compliant municipal water supply district. Despite notification to the community, it is possible that a few shallow unpermitted (and infrequently used) irrigation wells may be present in the neighborhood. An additional concern is the impact of offsite contamination to residential property values. Given a depressed local housing market, separating real and perceived property value impacts is difficult. Currently there is no active use of the industrial property. Another community concern is the inactive nature of the former industrial property.

Mapping Contaminant Distribution and Fluxes -

Figure 51 presents a 14 Compartment Model OoM depiction of the contaminant distribution before and after 10 years of hydraulic control. Before and after conditions

are depicted in the columns labeled “before” and “after.” The following variations from the standard 14 Compartment Model have been employed:

- Six separate compartment models have been employed for different parts of the plume.
- Since DNAPL is not present, rows with the DNAPL have been eliminated.
- There are no consequential transmissive zones in the deep lacustrine clay; hence, columns for transmissive zones have been eliminated in the deep plume compartment models.

Both “before” and “after” conditions are based on field data. The technology rating “Tech” is based on the observed difference between “before” and “after” conditions. This presents another novel application of the 14 Compartment Model. It can be used to develop site-specific maps of technology performance based on observed “before” and “after” conditions. As a check, the observed performance “Tech” of hydraulic control is similar to the general analysis of the performance of hydraulic control presented in Section 4.

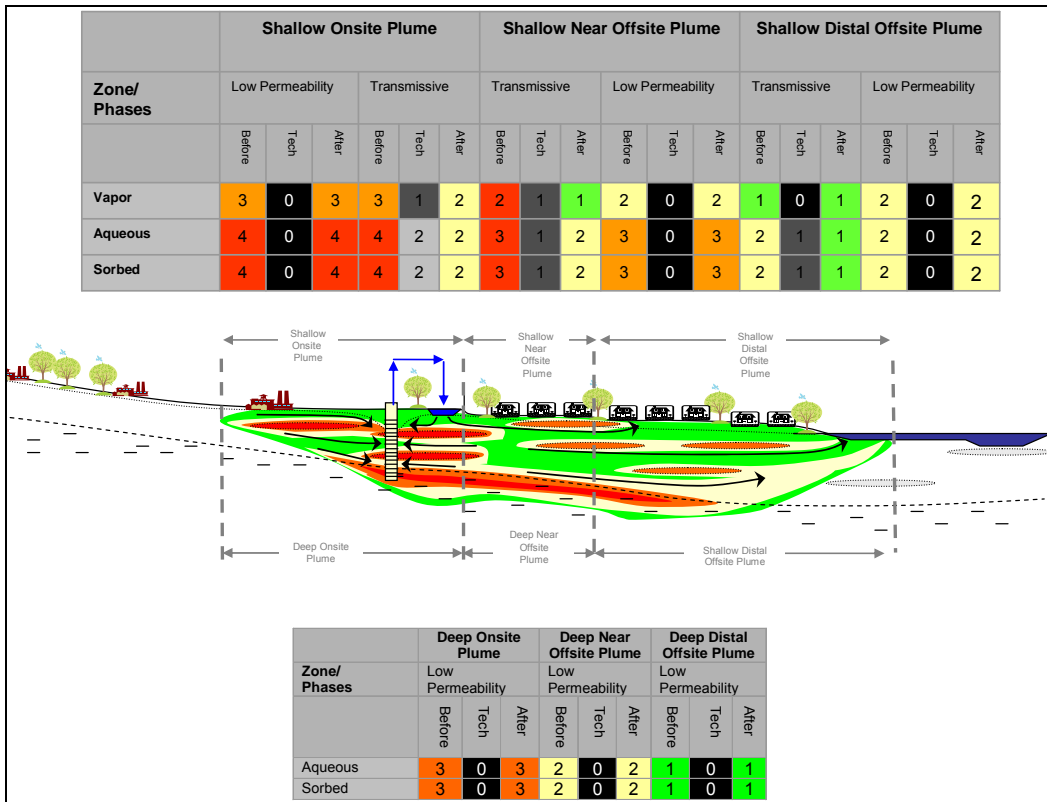


Figure 51 - Cross-sectional representation with 14-compartment mapping of Example Site 2. “Before” and “After” depicts observed conditions before and 10 years after hydraulic control. In this example the Technology Performance “Tech” was not estimated, but

calculated based on actual knowledge of “Before” and “After” concentrations in the transmissive compartments.

Per the terminology introduced in Section 2:

- Both the shallow and deep plumes are late-stage scenarios
- The shallow plume is in a Type III geologic setting
- The deep plume is in a Type II geologic setting

In more detail, the “before” and “after” mappings of contaminant distribution in

Figure 51 were developed by first looking at available water quality and soil gas data. This information was used to inform the aqueous and vapor phase concentrations in transmissive zones. The remaining compartments were filled in based on anticipated partitioning between phases and transmissive and low permeability zones per the processes described in Section 2. Unfortunately, as was the case in the first example, no data was available from low permeability zones. For sites where critical information is missing efforts should be made to collect the information needed to make fully informed decisions. Again, attempts to fill in the 14 Compartment model can help inform site managers where they are lacking key data, such as concentrations of contaminants in low-permeability zones.

Last, Figure 45 also shows compartments where human exposure seems most likely to occur (offsite indoor air - house icon and groundwater well - icon). As with the first example, the 14 Compartment Model is used to resolve exposure pathways. Critically, in this example, discharge of chlorinated solvents to surface water is not a primary concern. For this example, limited concerns with site related impact to surface water reflects other, more significant, water quality issues in the surface water body.

Objectives

Next, a “first cut” set of absolute and functional objectives are advanced for the site. As described in Section 3, should any of the functional objectives prove to be unattainable, an option for subsequent iterations is to replace the functional objective with a refined objective of equal value that is attainable. Key drivers for stakeholders at Example Site 2 are:

- Locally, homeowners in the residential area are concerned about potential health effects, potential impacts to property values, and undue disruptions in the neighborhood.
- Regionally, the community is committed to a clean environment while wanting to find new uses for closed industrial properties in the area.
- The facility owners are committed to immediately addressing any complete exposure pathways and meeting all other obligations within the constraints of:
 - A preference for actions that have consequential benefits
 - Working within the bounds of what is economically feasible
 - A preference for solutions with low operations and maintenance requirements.
- Regulators wish to support the interests of the community, provide technical support to all parties, and pursue compliance with applicable rules and regulations.

Building on the discussion of absolute objectives presented in Section 3, our hypothetical (envisioned mutual consent) absolute objectives are:

- Protection of human health and the environment
- Address adverse community impacts
- Conservation of natural resources

Hypothetical functional objectives are presented in the first column of Table 7. Additional columns in Table 7 to the right of the functional objectives, provide a basis for qualitative ranking of how well a select action or set of actions meets the desired result in the near term (a few years) or long term (a decade or more). Inclusive to the option is the status quo. For this example the status quo includes:

- Continuation of the hydraulic containment
- Maintaining vapor mitigation systems
- Monitoring

The adjacent image provides an OoM rating system for attainment of functional objectives. The OoM attainment rating system is applied for the status quo in Table 7. Pragmatically, any new set of actions should result in a consequential improvement over the status quo.





OoM Ratings for Attainment of Functional Objectives	
	Favorable attainment
	Cautionary partial attainment
	No clear benefit
	Concerns regarding adverse outcome

Table 7 – Functional objectives and *status quo* rating for Example Site 2

	Status Quo	
	Short	Long
Term in which the result is anticipated		
Risk		
Mitigate adverse human exposure via soil gas	Yellow	Yellow
Mitigate adverse human exposure via groundwater	Yellow	Yellow
Avoid actions that have the potential to increase risk	Yellow	Yellow
Extent		
Reduce the extent of plumes	Grey	Grey
Longevity		
Reduce the period in which persistent releases to groundwater occur	Grey	Grey
Reduce the period in which persistent releases to soil gas occur	Grey	Grey
Regulatory		
Comply with local, state, and federal regulations	Grey	Grey
Community		
Avoid undue interruptions to community	Green	Green
Address concerns regarding impacts to offsite property values	Grey	Grey
Land use		
Restore beneficial use of the former industrial property	Grey	Grey
Economic		
Employ actions that have practical near-term capital costs	Grey	Grey
Employ actions that have practical operations and maintenance costs	Grey	Grey
Sustainability		
Employ measures that have a net positive environmental benefit	Grey	Grey
Implementation		
Employ remedies that are practical to implement	Yellow	Yellow

Advancement of a Package of Remedial Measures

As with Example 1, advancement of a package of remedial measures is envisioned as an iterative process in which options are proposed, performance is anticipated relative to functional objectives, and complementary measures are added in an attempt to address limitations. The overall vision is that all parties with relevant interests should participate in roles that are appropriate for their interests and abilities. The first step in this process is resolving a “first cut” set of actions that are given and, conversely, actions that are unlikely. For this example:

- Given
 - Land use restrictions that preclude future use of groundwater in the impacted area for the foreseeable future.
 - Maintenance of vapor mitigation on all homes where there is a potential for adverse site-related indoor air exposures, for as long as the problem exists.
 - Monitoring to verify the protectiveness of the site remedy.
- Unlikely
 - Based on costs, traffic, and sustainability concerns, onsite or offsite excavation or thermal treatment of impacted media.
 - Any major construction or operations in the residential area, based on unacceptable interruption to life in residential areas. This includes:
 - Close center (30-foot spacing) injection of treatment media (e.g., oxidants) in residential areas.
 - Installation of continuous reactive barriers along residential streets.
 - Installation of groundwater extraction systems.

Primary concerns with the current hydraulic containment system include:

- As configured, groundwater extraction creates hydraulic stagnation zones in portions of the downgradient residential areas. Correspondingly, in low flow areas, slow release of contaminants from low permeability zones, without active flow, appears to be leading to elevated vapor and groundwater concentrations.
- The hydraulic containment system requires a high level of effort, requires a large amount of energy, and discharges vapor phase chlorinated solvents to the atmosphere. From a sustainability perspective, the current hydraulic control system is viewed as a marginal solution.
- It seems unlikely that hydraulic control will have consequential benefits in terms of indoor air concerns (the biggest issue) in any reasonable period of time.

For our hypothetical example we assume that the interested parties propose two options:

- **Iron PRB** - Replacing the current hydraulic control system with an iron PRB along the downgradient edge of the property.
- **Hydraulic Barrier with Hydraulic Control** - Placement of a sheet pile wall (low flow barrier) between the extraction wells and the recharge pond. This will limit circulation of treated water back to the recovery wells while enhancing the flushing of clean water into offsite plumes.

The vision for both of these remedies is to continue to sustain a near zero flux of contaminants at the downgradient site property boundary, increase the flushing of contaminants from beneath downgradient residences, emplace a layer of fresh water (no TCE) beneath the homes to reduce the flux of TCE from groundwater to vapor, and continued slow natural attenuation of TCE in transmissive and low permeability zones. Therefore the analysis of both alternatives using the 14 Compartment Model (Figure 52) is identical. (Note the illustration shows the cutoff wall with hydraulic control option). From an OoM performance perspective, an almost identical result is anticipated for the iron PRB option when evaluating performance (Figure 51).

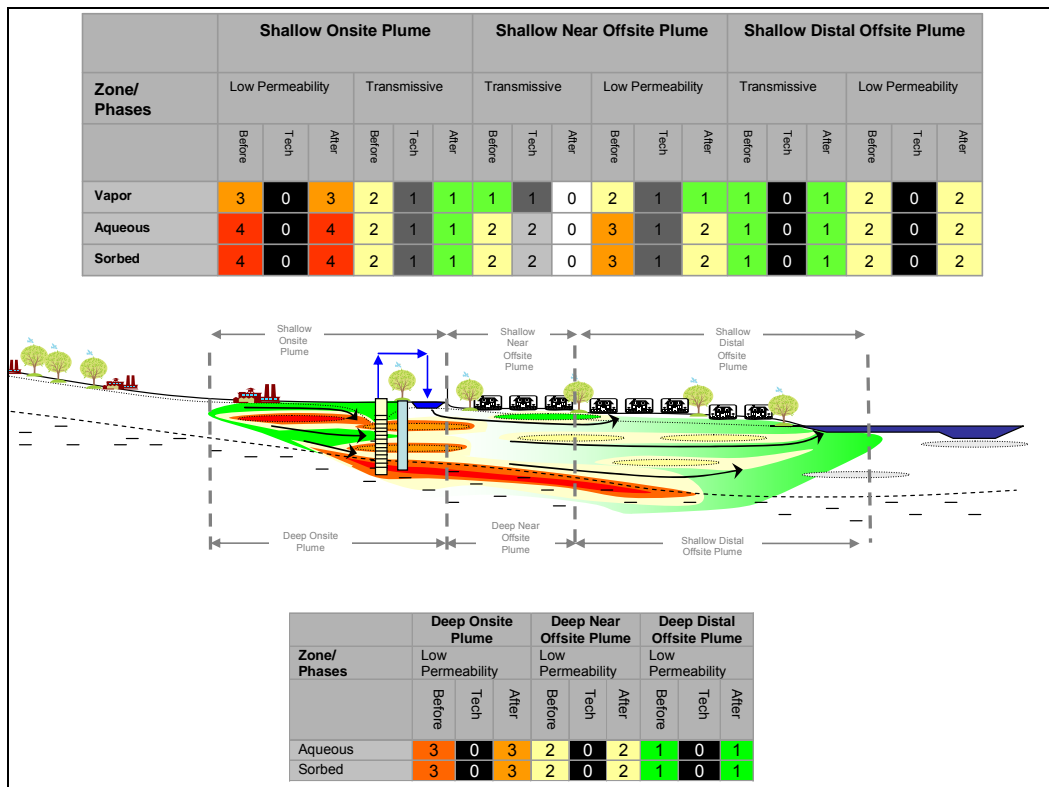


Figure 52 – Near term (~5 years) effect of an iron PRB or a Hydraulic Barrier with hydraulic control at the property boundary.

Table 8 outlines how the options perform relative to the functional objectives. Given the results, limitations to the options include:

- Given a natural gradient, large periods of time will be required to flush consequential amounts of “clean water” into the offsite plumes.
- Per the above point, an extended period of time will be required to reach numerical cleanup standards.

- Concerns with site-related impacts to offsite property values and the inactive nature of the industrial property are largely unaddressed.
- In the case of the hydraulic barrier with hydraulic control:
 - Long-term operation is a chronic burden.
 - Air stripping, leading to discharge of chlorinated solvents to air, remains a concern.

Table 8 – Example 2 - Functional objectives and rating for status quo, iron PRB and hydraulic barrier with hydraulic control

	Status Quo		Iron PRB		Hydraulic Barrier with Hydraulic Control	
	Short	Long	Short	Long	Short	Long
Term in which the result is anticipated						
Risk						
Mitigate adverse human exposure via soil gas						
Mitigate adverse human exposure via groundwater						
Avoid actions that have the potential to increase risk						
Extent						
Reduce the extent of plumes						
Longevity						
Reduce the period in which persistent releases to groundwater occur						
Reduce the period in which persistent releases to soils gas occur						
Regulatory						
Comply with local, state, and federal regulations						
Community						
Avoid undue interruptions to community						
Address concerns regarding impacts to offsite property values						
Land use						
Restore beneficial use of the former industrial property						
Economic						
Employ actions that have a practical near-terms capital cost						
Employ actions that have practical operations and maintenance costs						
Sustainability						
Employ measures that have a net positive environmental benefit						
Implementation						
Employ remedies that are practical to implement						

Building on the Table 8 analysis, the following modifications to the iron PRB and hydraulic barrier with hydraulic control options are proposed:

- For both options:

- Surface remnants of the industrial facility will be removed and the property will be converted to open space with restored natural areas, bike trails, recreational fields, select deed restriction. This addresses concerns regarding inactive land in the neighborhood and should enhance local property values.
- For hydraulic barrier with hydraulic control:
 - Supplemental clean water will be added to the recharge ponds to enhance the rates of freshwater emplacement in the offsite plume.
 - The air stripping water treatment system will be replaced with activated carbon. Furthermore, the owner will explore the use of emerging water treatment technologies that hold promise of lower cost and/or greater sustainability.

Furthermore, given the implausibility of near-term attainment of numerical cleanup levels in the plumes, the regulatory functional objective is proposed to be modified as follows:

Comply with local, state, and federal regulations → Given ongoing progress, site-related concentrations of TCE in wells (constructed in transmissive zones) and indoors should comply with health-based standards in 40 years.

Clearly, this proposal represents a difficult dilemma, and may not be acceptable. This dilemma is common at chlorinated solvent sites, and regulators continue to struggle with the implications of the technical difficulties involved in near-term attainment of numerical criteria (an important ongoing effort is the ITRC Integrated DNAPL Site Strategies team - http://www.itrcweb.org/teampublic_IDNAPLSS.asp).

Summary - Table 9 presents the performance of the enhanced remedies (labeled with “plus”) against modified functional objectives. For the purpose of this example, we assume that hydraulic barrier with hydraulic control plus is selected, based on better overall performance relative to the functional objectives. With this remedy all parties get a consequential improvement over the status quo. On the other hand, all parties have also found room for compromise. Specifically:

- Residents have accepted a long-term solution.
- Regulators have allowed an extended period to achieve their goals.
- Owners have committed to further investments.

Table 9 – Example 2 - Functional objectives and ratings for status quo and options

	Status Quo		Iron PRB Plus		Hydraulic Barrier with Hydraulic Control Plus	
	Short	Long	Short	Long	Short	Long
Term in which the result is anticipated						
Risk						
Mitigate adverse human exposure via soil gas	Yellow	Yellow	Yellow	Green	Green	Green
Mitigate adverse human exposure via groundwater	Yellow	Yellow	Yellow	Green	Green	Green
Avoid actions that have the potential to increase risk	Yellow	Yellow	Green	Green	Green	Green
Extent						
Reduce the extent of plumes	Grey	Grey	Grey	Yellow	Yellow	Green
Longevity						
Reduce the period in which persistent releases to groundwater occur	Grey	Grey	Grey	Yellow	Yellow	Green
Reduce the period in which persistent releases to soils gas occur	Grey	Grey	Grey	Yellow	Yellow	Green
Regulatory						
Given ongoing progress, site-related concentrations of TCE in wells (constructed in transmissive zones) and indoors should comply with health-based standards in 40 years	Grey	Grey	Yellow	Yellow	Yellow	Green
Community						
Avoid undue interruptions to community	Green	Green	Green	Green	Green	Green
Address concerns regarding impacts to offsite property values	Grey	Grey	Yellow	Green	Green	Green
Land use						
Restore beneficial use of the former industrial property	Grey	Grey	Green	Green	Green	Green
Economic						
Employ actions that have a practical near-term capital cost	Grey	Grey	Grey	Grey	Yellow	Yellow
Employ actions that have practical operations and maintenance costs	Grey	Grey	Green	Green	Grey	Yellow
Sustainability						
Employ measures that have a net positive environmental benefit	Grey	Grey	Yellow	Yellow	Yellow	Yellow
Implementation						
Employ remedies that are practical to implement	Yellow	Yellow	Green	Green	Yellow	Yellow

Example 3 –Release of TCE in a Regional Water Supply Aquifer

Site Conceptual Model

Background - Example 3 involves a 1950s-70s era aircraft maintenance facility where TCE was used in manufacturing activities. As with Example 2, industrial process waters were conveyed via sewers to a pond with no discharge points. Influent flows to the pond were accommodated by evaporation and seepage losses. Seepage losses were on the order of 100s of thousands of gallons per day. Given the operations, much of the TCE released occurred as an aqueous phase driven by recharge water. In addition, some of the TCE was released as a DNAPL. The site overlies a prolific deep regional alluvial groundwater basin. Large amounts of groundwater are produced for agricultural irrigation in the local area. Furthermore, local small- and medium-sized communities rely on deep groundwater for water supply. Regional consequences of deep groundwater production include large vertical gradients and groundwater levels that have fallen 50 feet over the past 40 years.

Figure 53 illustrates the site setting. Key features include:

- An interconnected matrix of low permeability silts and clay that contain secondary permeability features including fractures, root casts, and animal burrows. The matrix is shown in gray. Continuous white lines through the gray represent secondary permeability features within the low permeability body. Following Section 2 terminology, this is a Type V geologic setting.
- Interbedded aerially extensive transmissive layers consisting of poorly sorted sands and gravels with small-scale interbeds of low permeability silt. The transmissive zones are shown in white with small gray low permeability interbeds. Following Section 2 terminology, this is a Type III geologic setting.
- A deep pumping well located one mile downgradient of the site.
- A set of compartment models depicting conditions that are anticipated to have existed during the initial TCE release.

High oxidation-reduction potential (ORP) and the absence of TCE degradation products in groundwater suggest that little if any natural attenuation of chlorinated solvents is occurring.

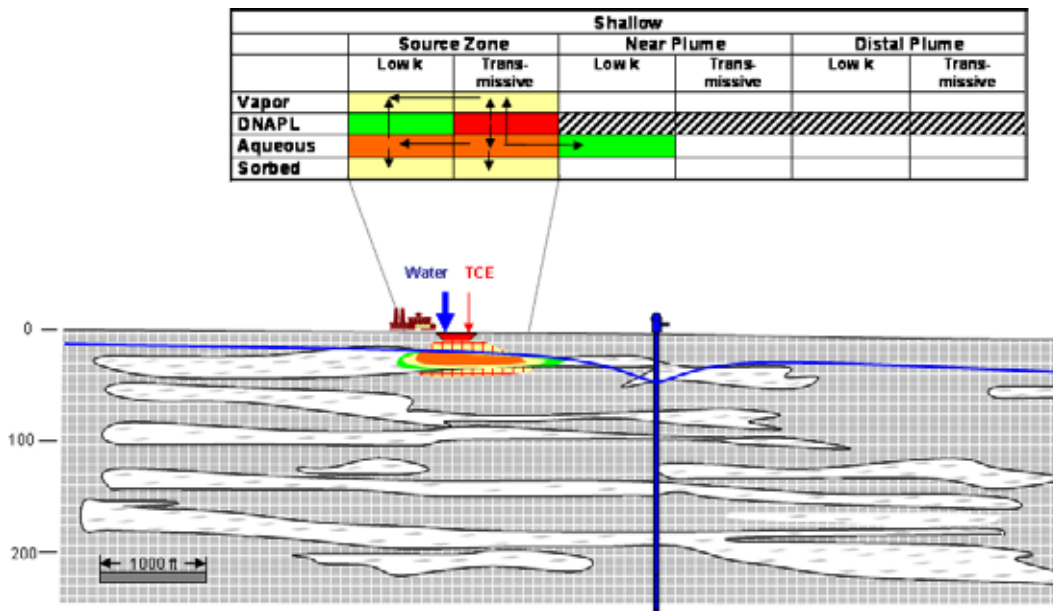


Figure 53 - Example 3 - Site setting with the anticipated contaminant distribution early in the release (1960s).

In 1980 onsite use of TCE ended. From 1980-2010 a comprehensive set of measures were undertaken including:

- Shutdown of the well shown in Figure 53 due to TCE contamination.
- Excavation of impacted soils beneath the pond.
- Soil vapor extraction in the uppermost transmissive layer near the former pond.
- 30 years of aggressive multiple-well offsite extraction and treatment of impacted groundwater.
- Replacement of a potentially threatened municipal well field with a new (remote) well field.

Conditions prior to the above actions (1980) are depicted in Figure 54. Through the noted actions, approximately 20 tons of TCE were removed from the subsurface. The distribution of contaminants in 2010, after the above actions, is depicted in Figure 55. Inclusive to Figure 55 is a set of compartment models depicting conditions before (1980) and after (2010) 30 years of aggressive remediation.

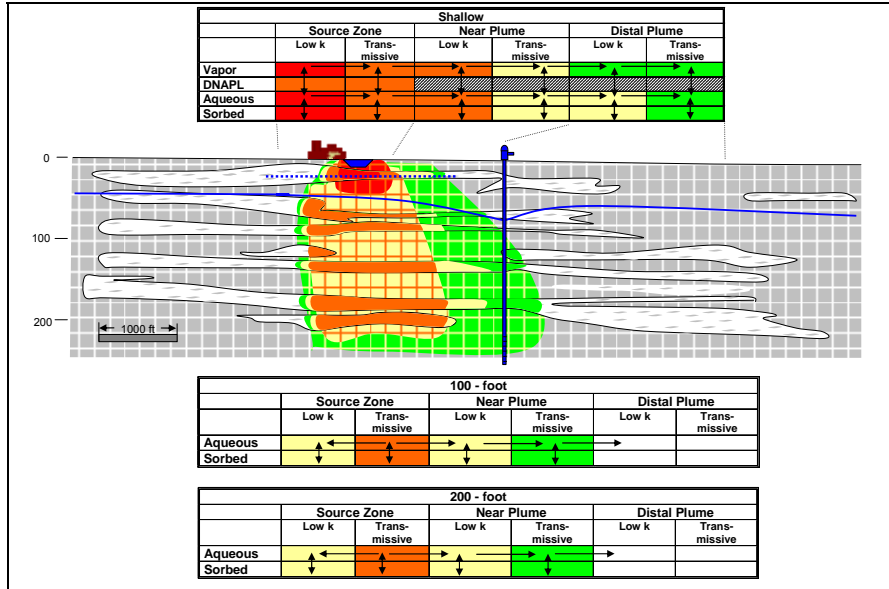


Figure 54 - Pretreatment conditions (1980s).

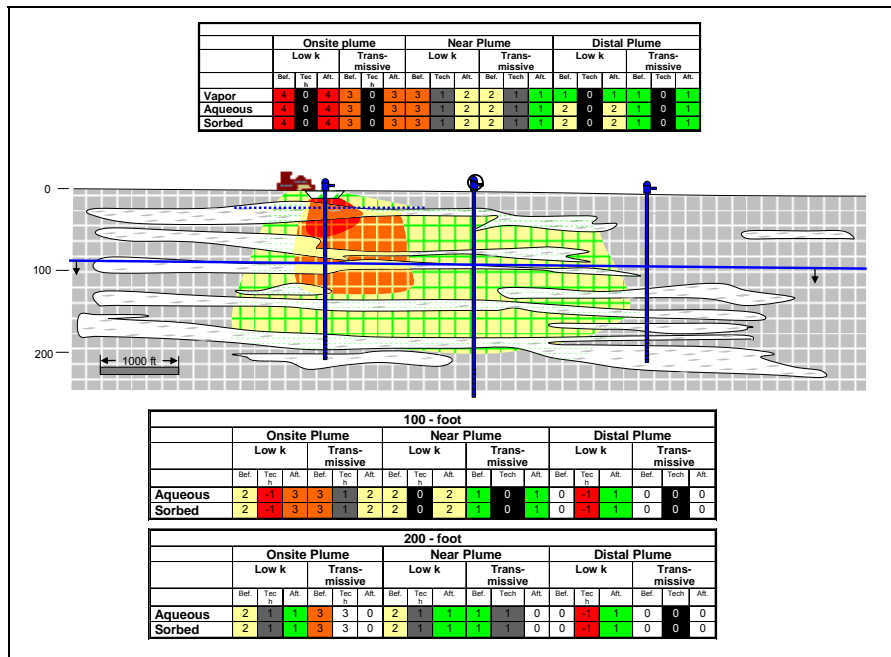


Figure 55 - Conditions after 30 years of active remediation (2010)

As was done in Example 2, the difference in OoM contaminant concentrations before and after remediation is used in Figure 55 to develop OoM ratings for the remedial actions. Results include:

- A three OoM improvement in deep aqueous phase concentrations in transmissive zones onsite.
- One OoM improvements in portions of the shallow and deep plume
- No consequential decrease in the source zone.
- One OoM increases (shown in red) in:
 - Deep portion of the distal plumes due to shutdown of the downgradient well that was containing the plume.
 - Low permeability zones in the source zone due to ongoing inward diffusion of TCE into the matrix in the low permeability zones.

While the above could be perceived as marginal progress, it is important to note that offsite groundwater contamination has been limited (for the most part) to levels near drinking water standards (1s of ug/L). In the absence of the actions, current conditions would likely be far worse.

By far, the primary concern of the community is sustaining groundwater-based irrigation agriculture. With this, key drivers are a) managing groundwater quality issues that could constrain use, and b) minimizing unproductive uses of groundwater that could lead to further declines in water levels. There are no residences above the plume and consequentially, no vapor intrusion concerns. Also, there is no local use of impacted groundwater for drinking water.

Objectives

Key drivers for stakeholders at Example Site 3 are:

- Driven by the community's reliance on irrigation agriculture, local interests want to reduce unproductive use of groundwater (limiting future declines) and preserve water quality that is consistent with the needs of irrigation agriculture.
- After 30 years of chronic investment, the former owners of the facility are anxious to move to a final solution for the site so they can better focus on their business. At the same time, the owners are committed to meeting all real obligations related to their past operations.
- Regulators wish to support the interests of the community, provide technical support to all parties, and pursue compliance with applicable rules and regulations.

Hypothetical absolute objectives for Example Site 3 are:

- Protection of human health and the environment.
- Addressing adverse community impacts.
- Conservation of natural resources.

Hypothetical functional objectives are presented in Table 10. Also presented is an analysis of the status quo. For this example the status quo includes ongoing extraction of groundwater and monitoring.

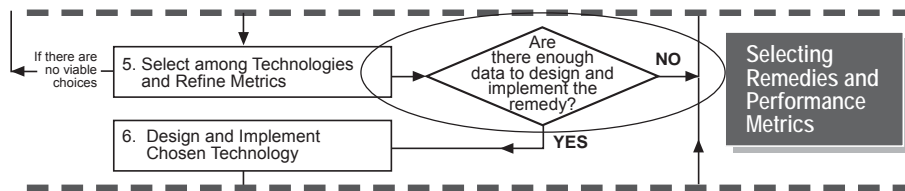
Table 10 – Functional objectives and status quo rating for Example Site 3.

	Status Quo	
	S h o r t	L o n g
Term in which the result is anticipated		
Risk		
Mitigate adverse human exposure via soil gas		
Mitigate adverse human exposure via groundwater		
Avoid actions that have the potential to increase risk		
Extent		
Reduce the extent of plumes		
Longevity		
Reduce the period in which persistent releases to groundwater occur.		
Regulatory		
Comply with local, state, and federal regulations		
Community		
Limit unneeded withdrawal of groundwater		
Maintain groundwater quality consistent with agricultural use		
Economic		
Employ actions that have a practical near-term capital cost		
Employ actions that have practical operations and maintenance costs		
Sustainability		
Employ measures that have a net positive environmental benefit		
Implementation		
Employ remedies that are practical to implement		

Advancement of a Package of Remedial Measures

Given the analysis in Table 10, it is envisioned that all parties agree that it would be desirable to move toward a more passive site management strategy so long as it is protective of human health and compliant with regulatory requirements. The primary hurdle to this vision is that there is potentially enough TCE remaining in low permeability

portions of the source zone (despite partial excavation and SVE) to act as a chronic source (see Figure 55). Per Section 4, two potential options for treatment of contaminants in low permeability source zones are conductive heating and ZVI-Clay. Given depths and volumes, both these options are likely to have costs on the order of tens of millions of dollars. Unfortunately, historical site characterization based on water quality in wells with long screen interval provides little if any insight regarding the true presence and potential consequences of contaminants stored in low permeability zones. Given this, it is envisioned that all parties would agree that characterizations of low permeability zones using high resolution techniques would be warranted prior to selecting a remedy. Following the work of Dr. Beth Parker at the University of Guelph, the high resolution technique for low permeability zones includes collection and analysis of continuous core, use of the Waterloo Profiler, and/or use of Membrane Interface Probe systems (MIPs). This scenario illustrates the “collect data” option as a precursor to making decisions, as illustrated below (from NRC, 2005):



Last, prior to proceeding with further work, it is envisioned that all parties would need to discuss whether further partial removal of TCE could lead to a final passive site care strategy or simply to yet another element of a Sisyphean task.

Section 6 - Limitations

The authors wish to acknowledge the limitations of this document. Many of these are described in the text Sections 1-5. In addition, we would like to highlight four critical issues.

Project Scope

When this project was initiated the idea of developing the ***Frequently Asked Questions Regarding Management of Chlorinated Solvents in Soils and Groundwater*** seemed quite reasonable. In fact, this turned out to be true. On the other hand, success with development of ***A Guide for Selecting Remedies for Subsurface Releases of Chlorinated Solvents*** seemed less plausible. Constraints included the modest project budget, the complexity of the problem, and limited progress that had been made by more austere groups facing the same questions (i.e. USEPA 2003 and NRC 2005). Nevertheless, ESTCP and the project team agreed that an attempt at developing a Decision Guide would be worthwhile if it only to set a foundation for future efforts. In this regard we feel we have succeeded.

Specifically, this document sets a foundation for better use of finite remediation resources, more effective risk management, and more productive cooperation between the parties involved in site cleanups. We hope others will build on this foundation with the benefits of a cleaner environment and the opportunity for DoD and others to better focus on their core missions. At the same time this document is far from perfect. Areas for further work are noted in the remaining portions of this section.

Governing Processes

The field of contaminant transport in natural porous media is a relatively new. This is reflected in FAQ 10 (What have we learned over the last half century?). Many of the historical tenants of our profession (i.e. land disposal of waste solvents) have proven to be flawed. It would be presumptuous to assume that we now (in this document) have contaminant transport and remediation “all figured out”. Almost certainly, a few more surprises lie before us. We encourage readers of this document to consider our ideas,

remain up-to-date on emerging thinking, and recognize the need for independent thinking.

Performance of Remedial Technologies

Chapter 4 anticipates the performance of a wide range remedial technology. Our analysis, for pragmatic reasons, is predicated on a limited review of available data. Users of the document are encouraged to seek out other knowledge regarding the performance of remedies. One of the most promising sources of additional information is ESTCP project ER-200424 - Development of a Protocol and a Screening Tool for Selection of DNAPL Source Area Remediation. User of this document should look to the final report for ER-200424 (anticipated in 2011) for additional information regarding the performance of remedies in different hydrogeologic setting.

The 14 Compartment Model

The needs of this project drove us to develop the “14 Compartment Model”. Initially the 14 Compartment Model provided a holistic foundation for tracking four phases of chlorinated solvents that can occur in transmissive and low k zones, in source zones and plume. Subsequently, additional niches were found for the 14 Compartment Model including mapping fluxes between compartment, analysis of the aging of release, generic mapping the performance of technologies, identifying data gaps, and anticipating the outcomes of remedies at individual sites. In all of this the 14 Compartment Model provides a relatively simple tool manage complex issues and interactions. At the same time, it is important to note that the 14 Compartment Model is a highly idealized simplification of the real systems we deal with. Key limitations include:

- **Contaminant Concentration vs Contaminants Mass** - The model relies on concentrations to evaluate alternatives and impacts on various compartments. It needs to be pointed out that a sound conceptual site model sound should also consider the masses of contamination in all of the relevant compartments. The 14-Compartment Model's concentration-based can be misleading if it is not used in conjunction with a mass-based site model.
- **Only an Element of a Site Conceptual Model** - It is important to point out that the model is a tool for aiding decision-making, and should be based on a comprehensive conceptual site model that includes mass balances, the spatial distribution of mass, the site hydrogeology, and the mass discharge and mass flux distribution. The 14 Compartment Model is simply a potential part of a site conceptual model.

- **Uncertainty** - Care is needed in recognizing uncertainties in 14-Compartment Model entries. This particularly true for compartments where little or no hard field data is available. For example, in many cases the little to no data may be available from low permeability zones.
- **Oversimplification** - Regardless of the scale of analysis the 14 Compartment Model simplifies systems. Care is needed in not ignoring details that may be consequential to the outcomes of proposed remedies.

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