

## Remediation of Complex Chlorinated Solvent Sites While Maximizing Return on Remediation Investment

*Eliot Cooper, Director Combined Remedy Strategies, Gorm Heron, Chief Technology Officer, Neil Hey, Program Manager and National Bioremediation Lead, Karen Suchomel, Key Accounts Manager*

### 1. Introduction

As the environmental remediation industry matures, the focus of technological advancement has shifted to addressing the remaining “complex sites”. The National Research Council (NRC) (2005) estimated that more than 126,000 sites have residual contamination preventing them from reaching closure and of those, 12,000 sites have residual contamination that will require between 50 to 100 years to achieve restoration, at an estimated cost of between \$110 to \$127 billion dollars. Many complex sites are characterized by persistent chlorinated solvent impacts that for various reasons have not responded to traditional or simplistic technologies. In these cases, achieving a positive return on remediation investment (RORI) should be considered as a factor in evaluating the overall existing and future remediation approaches. RORI at a complex site is not optimized merely through technology selection but rather by designing an overall process to manage restoration from characterization through remedy implementation.

The total life cycle cost (TLCC) for a remediation project consists of:

$$\text{Characterization Cost} + \text{Remediation Cost} + \text{Transition Assessment Cost} + \text{Long-Term Management Cost} = \text{TLCC}$$

Therefore, we define RORI as the design pounds of the contaminant of concern (COC) to be treated or removed as a part of the overall cleanup strategy per dollar spent:

$$\text{RORI (\%)} = \text{Lbs COC Removed} * \text{TLCC} / \text{Design Lbs COC} * \text{TLCC}$$

*As remedies fail by not achieving the Design Lbs of COC, the RORI is reduced. Additionally, failing to transition to long-term management and possibly revisiting site characterization and remedies will also negatively impact RORI. More importantly delays result in increased TLCC costs as new COC standards maybe set, emerging contaminants may become mainstream and the plume increases in volume*

The library of lessons learned based on real-life application of available technologies has grown significantly over the last 20 years. Remediation progress at complex sites (and subsequently, the RORI) has been hindered by:

- Misunderstanding both the extent and/or distribution of chlorinated solvents in source zones and the technical limits regarding how accurately or completely a source zone can be characterized.
- Poor understanding of what technologies can effectively do, and reliance on singular remedies to address large source areas and plumes.
- Uncertainties or errors in remedy design and failure to learn from performance monitoring data to optimize the remedy.
- Inability to recognize when a change in remedy or transition to a passive remedy is warranted, or regulatory challenges that make changing remedies difficult and time-consuming.
- Remedial objectives that can only be achieved over a long period of time (such as maximum contaminant levels [MCLs]), without using other short-term objectives tied to remedy design and optimization.

However, we’ve also learned that it is possible to maximize RORI by:

- Setting realistic remediation goals.
- Collecting the right type and quantity of characterization data.

- Carefully selecting the appropriate remedy(ies) based on bench and design optimization testing.
- Applying best practices to implement remedies.
- Monitoring for the right type and quantity of performance data

This paper presents an overview of the current state of characterization and remediation science, and presents examples of how, by combining traditional and high resolution site characterization (HRSC) methods and targeted remedy options, consultants can achieve better results and provide greater value to their clients by maximizing RORI.

## 2. Current State of Innovative Remediation Approaches

The traditional approach to achieve site closure moves logically from site characterization through remedy design and implementation, followed by post-remediation monitoring and regulatory closure. This approach is typically not modified significantly for complex sites, many of which fall into the U.S. Environmental Protection Agency (USEPA) Superfund program regulated under the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA). Under CERCLA, remediation goals are focused on achieving MCLs and progress is evaluated based on this standard.

The 2013 NRC publication, “Alternatives to Managing the Nation’s Complex Contaminated Groundwater Sites”, recommends an alternative approach to evaluating remedy efficacy that focuses on achieving an asymptote or point of diminishing returns (Figure 1).

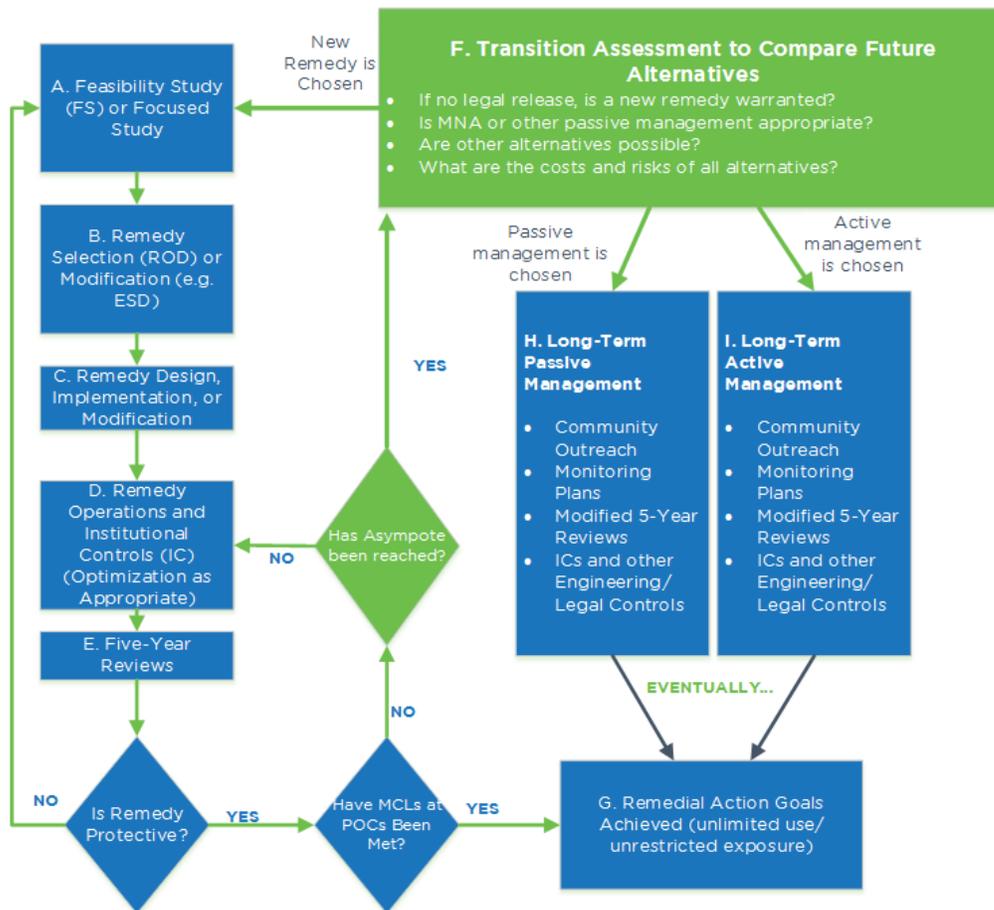


Figure 1 - Alternatives for Managing the Nation’s Complex Contaminated Groundwater Sites: NRC 2013

If an asymptote has been reached and remediation objectives have not been achieved, then the NRC recommends transitioning the remediation approach to include:

- Long-term active management of an operating remedy, plus appropriate monitoring, reporting, 5-year reviews, institutional or legal controls and community outreach; or
- Long-term passive management with no active remedy, reporting, 5-year reviews, institutional or legal controls, and community outreach. Consideration should be given to no additional monitoring, where appropriate.

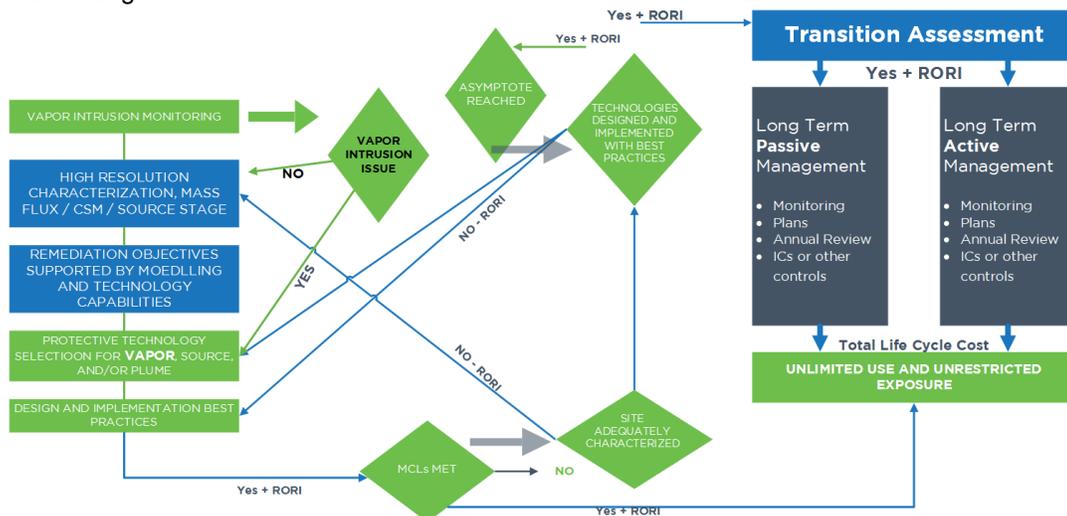
This shift reflects recognition that excessive remediation expenditures are not justified in situations where exposure risk is reduced to acceptable levels and additional progress towards goals is unlikely using currently available technologies. However, benefits from the remediation accomplished must be shown including:

- Reductions in groundwater or indoor air concentrations
- Shrinking of the dissolved plume footprint
- Reduction in source zone mass
- An increase in the beneficial use of the site and affected resources

### **3. Taking the NRC Approach to Another Level of Technology Performance Prior to Transition to Long-Term Management – Cascade’s RORI Approach (Figure 2)**

Cascade recommends an approach that goes one step further than the NRC’s, focusing on the adequacy of characterization to support a remedy design that includes one or more remedies used in conjunction to treat various impacted areas. Our approach also includes collecting adequate and targeted performance monitoring data to support the timely transition to long-term management (LTM). Experience shows that a more robust characterization effort improves conceptual site models and therefore focuses remedy design, which accelerates progress towards a passive, more cost-effective long-term solution for complex sites. Implementing these steps at project inception improves overall remedy efficacy, sustains RORI, and reduces the risk that regulators will not approve the transition to LTM. Additional front-end work can eliminate the need for additional characterization activities years into the project, and subsequently the need and costs associated with evaluating alternative active remedies, achieving additional regulatory approvals and implementing new remedies. More importantly, faulty conceptual site models lead to potentially larger liabilities as the plume migration may continue to spread.

Since vapor intrusion (VI) is now becoming more actively regulated as part of the overall remediation process, the approach below also includes a vapor intrusion characterization step which takes precedent over all the other steps due to the need to mitigate short-term acute health risks associated with TCE.



**Figure 2 - Cascade Remediation Methodology - RORI**

### 3.a. The Added Remediation Complexity of the New TCE Standard for Acute Exposures

In 2011, USEPA's Integrated Risk Information System (IRIS) program released an updated human health risk assessment of TCE (results summarized on <https://www.radata.com/images/vapor-intrusion.png>). As a result, both the cancer and non-cancer inhalation toxicity values (inhalation unit risk and reference concentration) for TCE were lowered. In 2015, USEPA submitted a draft rule to the White House Office of Management and Budget to add VI to the pathways evaluated under the Hazard Ranking Scoring (HRS) System for National Priority List (NPL) Superfund sites. The rule would ensure that health risks associated with the VI pathway are adequately addressed during Superfund remediation. Additionally, in 2015, USEPA released final technical guidance on assessing and mitigating the VI pathway from subsurface vapor sources to indoor air (OSWER, 2015, Figure 3)

We anticipate seeing increased costs for due diligence in real estate transactions, where additional VI investigation (with potential for more robust vapor sampling approaches, and mitigation [Figure 5, next page]) may be necessary. Potential responsible parties (PRPs) will see changes in site cleanup standards to include VI cleanup levels, which will increase the cost and timeframe of remediation. Additionally, many sites previously closed with subsurface contamination still in place are being reopened for further remediation, and CERCLA Decision Documents are being re-evaluated to address the VI potential and ensure remedies are protective of human health.

In 2006 the New York Department of Environmental Conservation began re-evaluating remedial decisions at 421 hazardous waste sites throughout the State ([http://www.dec.ny.gov/docs/remediation\\_hudson\\_pdf/der13.pdf](http://www.dec.ny.gov/docs/remediation_hudson_pdf/der13.pdf)).

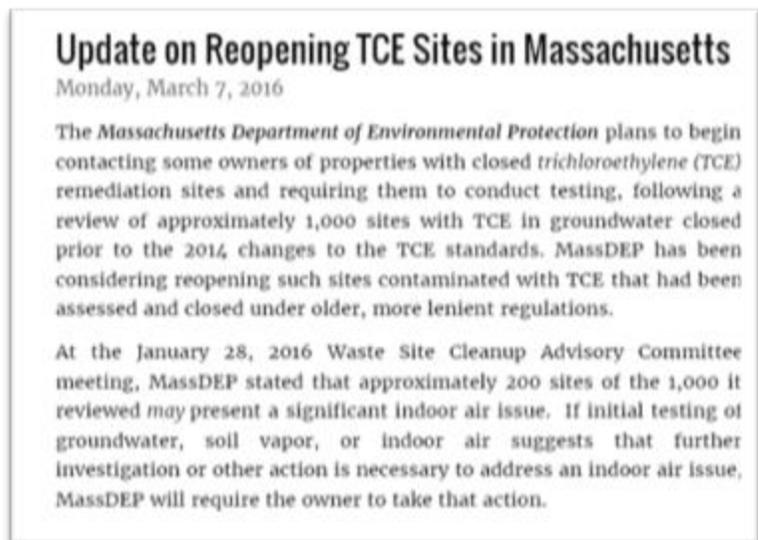
More recently, based on the new TCE Acute Risks, Massachusetts DEP has reopened 200 closed sites to assess whether the new TCE standards can be met (Figure 4).



**Short-Term TCE Exposure**

- Single (acute) or short-term exposure
  - Developing fetus - cardiac malformations
  - Critical period of exposure = 3 week period in 1st trimester when heart forming
  - Women in 1st trimester of pregnancy = most sensitive to TCE inhalation exposure
  - Concern is for all women of child bearing age

**Figure 3 - Short Term Acute Risks to Developing Fetus**



**Update on Reopening TCE Sites in Massachusetts**  
Monday, March 7, 2016

The Massachusetts Department of Environmental Protection plans to begin contacting some owners of properties with closed trichloroethylene (TCE) remediation sites and requiring them to conduct testing, following a review of approximately 1,000 sites with TCE in groundwater closed prior to the 2014 changes to the TCE standards. MassDEP has been considering reopening such sites contaminated with TCE that had been assessed and closed under older, more lenient regulations.

At the January 28, 2016 Waste Site Cleanup Advisory Committee meeting, MassDEP stated that approximately 200 sites of the 1,000 it reviewed may present a significant indoor air issue. If initial testing of groundwater, soil vapor, or indoor air suggests that further investigation or other action is necessary to address an indoor air issue, MassDEP will require the owner to take that action.

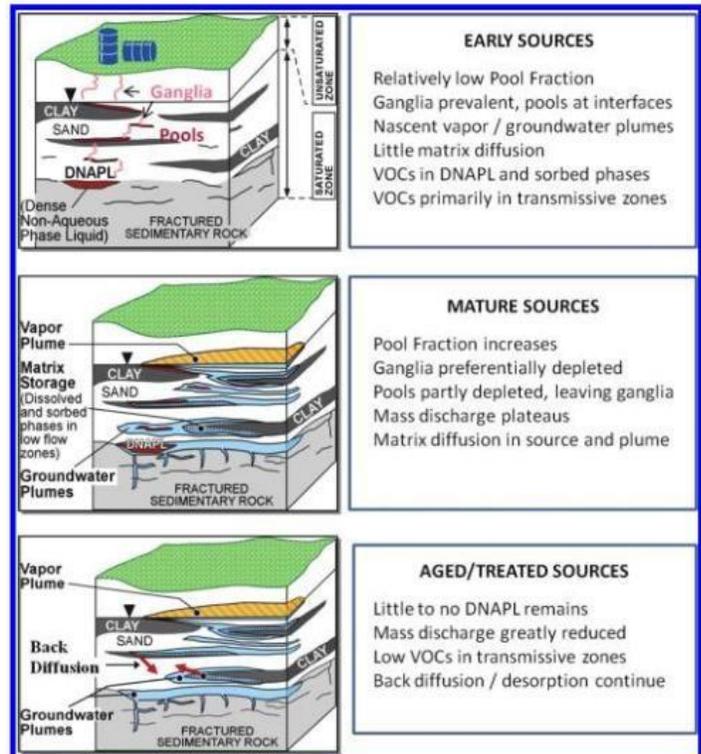
**Figure 4 - National Law Review March 7, 2016**

Region or State	Residential ( $\mu\text{g}/\text{m}^3$ )	Commercial ( $\mu\text{g}/\text{m}^3$ )
US EPA Region 9 (Accelerated/Urgent Response Levels)	2 / 6	8 / 24
US EPA Region 10 (Removal Action Level)	2	8.8
Massachusetts DEP (Imminent Hazard)	6	24
New Jersey DEP (Rapid Action Level)	4	18
New Hampshire DES (Action Level)	2	8.8
Cal/EPA DTSC (Accelerated Response Action Level)	2	8
Cal/EPA RWQCB-SF Bay Region (Accelerated Response Action Level)	2	8

**Figure 5 -Target TCE Indoor Action Levels**

### **3.b. Cascade’s Recommended Approach to Improve RORI: Comprehensive Characterization to Understand What Stage Your Site Is in and Potential for Matrix Back Diffusion**

**Understanding Contaminant Fate and Transport.** Chlorinated solvent releases involve heterogeneous distribution of DNAPL and other phases that are difficult to quantify. Reliance on data collected from wells with long screen intervals in transmissive zones provides little insight into distribution of DNAPL, sorbed phases and mass stored in low permeability zones. Mass can also be stored in the downgradient low permeability zones immediately beyond the “source” where DNAPL was originally present. Back diffusion from these reservoirs can sustain plumes long after the source has been treated. This insight has led to a conceptual model that can be useful in describing DNAPL sites because it illustrates potential technology limitations (Figure 6). Back diffusion can limit performance of any technology based on advective transport as contaminants in less permeable zones may remain untreated. Traditional characterization approaches illuminate only a portion of the problem. For example, data from monitoring wells show aqueous phase TCE in transmissive zones with concentrations averaged across the screened interval, however these data provide little insight regarding low permeability zones and/or other phases such as vapor (Figures 6, 7).



**Figure 6 - Evolution of DNAPL Source Zone and Key Features of Different Stages**

Abrupt contacts between transmissive zones and comparatively stagnant low permeability zones are common in geologic media. DNAPL or dissolved phase contamination initially moves preferentially through the pathway with the greatest permeability. With time, dissolved phase contaminants migrate into the low permeability layers via diffusion and/or slow advection. Contaminants in the clay layers are stored in dissolved and sorbed phase. Most natural processes and remediation technologies preferentially deplete chlorinated solvents in the transmissive zones. When this occurs, contaminants are then released from the low permeability zones via diffusion and slow advection.



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

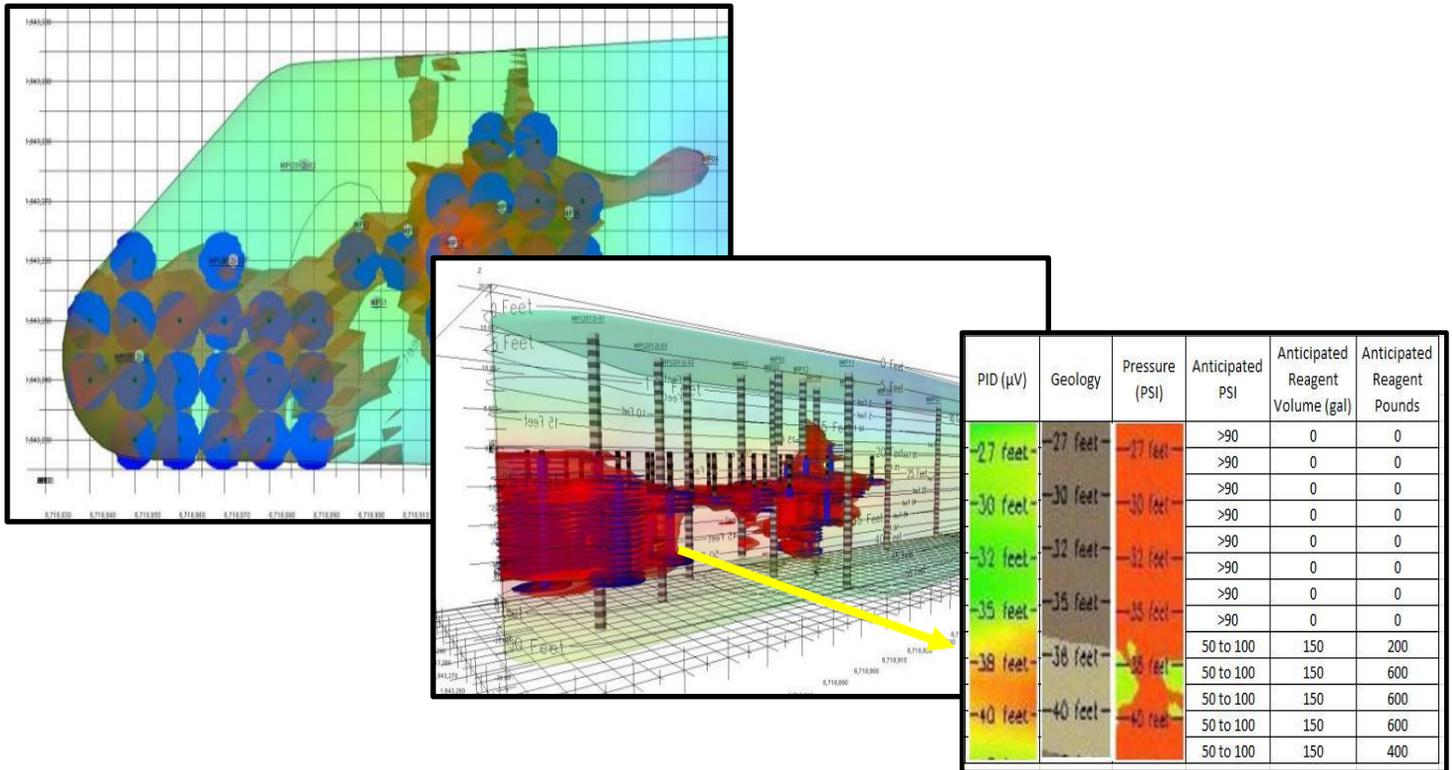
*Figure 7. Illustration of contaminant exchange between phases in source zones and plumes (Sales et al 2007) Solid Arrows depict reversible fluxes. Dashed arrows are irreversible fluxes. From Sale et. al, 2007*

### **3.c. Cascade’s Approach to Improve RORI: Comprehensive Characterization to Move Beyond Remedial Design Based Solely on Monitoring Well Data**

**Improve Site Characterization Utilizing HRSC Technologies.** Site characterization is often de-emphasized in a rush to install a source zone remedy. More often than not, the source zone is larger or distributed differently than originally thought, but this is realized only after initial remediation attempts, requiring iterative characterization and remediation, increasing costs and eroding the RORI.

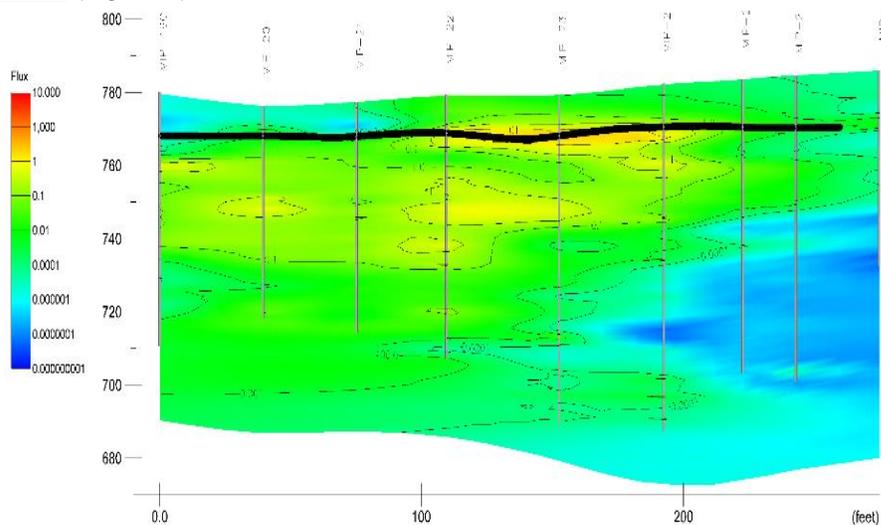
Modern site investigation techniques, such as the USEPA Dynamic Working Planning approach, ASTM expedited site characterization or adaptive site characterization, are faster, are less expensive, and produce better outcomes than conventional site investigations. Cascade offers a variety of specialized tools to optimize the amount and type of data collected to potentially customize the remediation design and footprint, increasing the probability of success and reducing execution costs.

- **Membrane Interface Hydraulic Profiling Tool (MiHPT):** The MiHPT is a rapid screening tool for locating volatile organic compounds (VOCs) in the subsurface, in both saturated and unsaturated zones. Unlike the more common MIP tool, it also collects hydraulic information such as downhole pressure and flow measurements that can be used to calculate relative hydraulic conductivity. When used in conjunction with an onsite analytical lab, MiHPT results allow a real-time estimate of the extent of contamination. 3D data interpretation and visualization software provide for targeted remediation recipes on a location-by-location basis (Figure 8).



**Figure 8 - 3D Imaged Targeted Injection Plan**

- Waterloo<sup>APS</sup> Profiler:** While the MiHPT provides relative VOC concentration data to determine plume configuration, once the plume anatomy has been defined, the Waterloo<sup>APS</sup> Profiler can obtain detailed, high-quality quantitative data on concentrations of particular analytes over high-density vertical intervals. Typically, contaminant mass discharge occurs over a small fraction of the total cross-sectional area of the plume suggesting that remediation can be targeted more effectively if high resolution sampling is conducted along one or more transects. These flux-based conceptual site models (CSMs) allow you to also focus on the mass that matters (Figure 9).

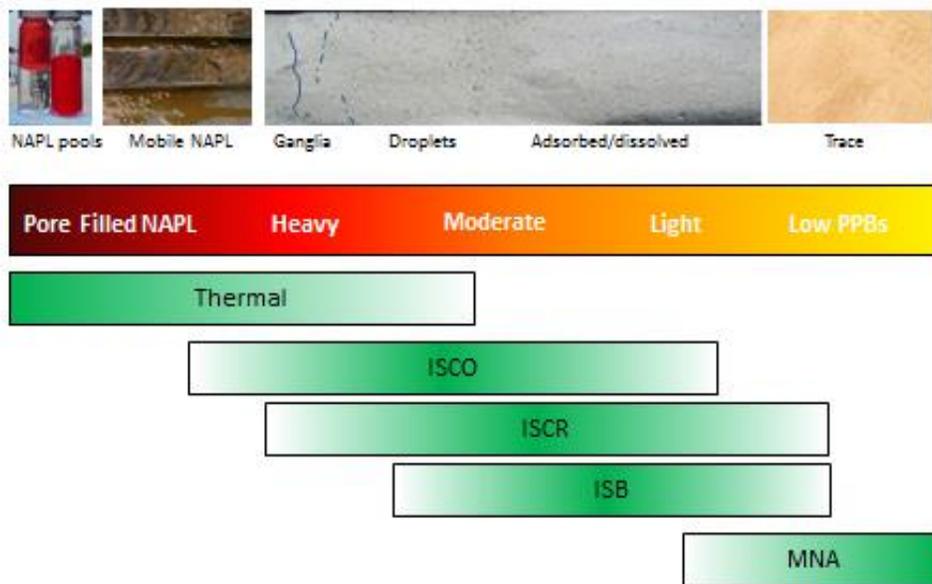


**Figure 9 – Example transect of groundwater TVOC flux based on Waterloo Profiler data. Units are ug/sec/cm<sup>2</sup>**

**4. Cascade’s Recommended Approach to Improve RORI: Optimize Source Area and Plume Remediation through Design and Implementation Best Practices and Combined Remedies**

In some cases, it is physically impractical to address a source zone (e.g., it is located under a building not accessible by interior or external horizontal drilling or in an ecologically sensitive area). Plume containment remedies such as hydraulic containment (pump-and-treat, permeable reactive barriers, etc.) are appropriate in these cases. However, these are very long-term solutions, and the pump-and-treat remedy has relatively high Total Life Cycle Costs and is not considered a green and sustainable option. Physical containment, such as a slurry wall, is also an option. The current body of evidence indicates that these options can be effective, but more often than not, fail due to a lack of understanding of the system hydraulics.

The past decade has seen rapid progress in source zone remediation and an increasing understanding of the capabilities and limitations of potential technologies. Technology-specific cost and performance reports can be found at <http://www.serdp-estcp.org/featured-initiatives/cleanup-initiatives/dnapl-source-zones>. Options offered to remediate source areas in situ include bioremediation, chemical oxidation, chemical reduction and thermal treatment. Typically, the nature and concentration of the contaminant of concern (COC) as well as the subsurface hydrogeology dictates which remedy is best suited for the site (Figure 10), though experience has shown that different technologies are needed at different times and locations, and combining technologies may improve overall remedy performance.



**Figure 10 - Recommended Technology Based on Contaminant Concentrations in The Target Zone**

The current state of the science for each remedy, including best practices for design and implementation, are discussed in the following sections. These are based on Cascade’s experience at hundreds of sites across the country with various subsurface geologic and hydrogeologic conditions and contaminant concentrations.

**4.a. Thermal Remediation.** Thermal technologies are used to treat heavily contaminated and complex sites where traditional mechanical, chemical or biotic approaches cannot be successful. Source zones with DNAPL are most often targeted for thermal treatment. Thermal is also attractive for treating sources in less permeable material (clays with high COC-sorbed mass) or in fractured media, where other in situ technologies face delivery challenges.

Thermal remediation is capable of removing greater than 99 percent of contaminants from even heavily contaminated source areas, but real-world performance can be impacted by site conditions (e.g. high groundwater seepage velocity > 1 ft per day) where thermal efficacy can be impacted by cooling caused by locally rapid groundwater fluxes.

Thermal remediation for VOCs is based primarily on:

1. Vaporization of NAPL, as the VOCs become volatile at elevated temperatures
2. Desorption and steam distillation, transferring the VOC into a steam phase
3. Hydrolysis for some alkenes

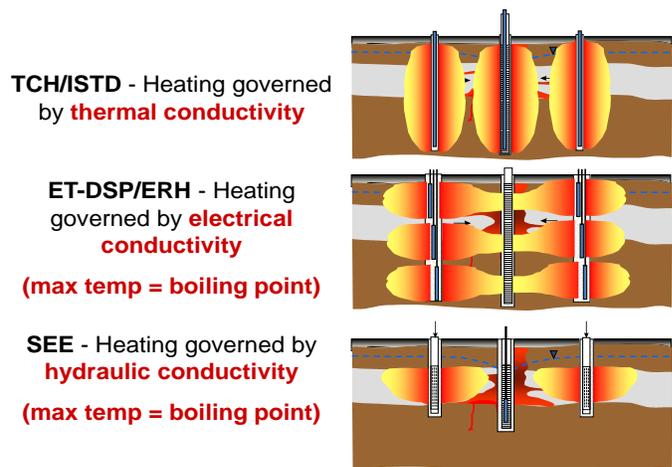
Thermal source treatment can be combined with other technologies to address contamination outside the thermal treatment zone, and in rare instances inside the treatment zone after thermal performance goes asymptotic (where extremely stringent criteria exist). Considerations include the following:

- In Situ Bioremediation (ISB) after thermal temperatures have cooled down to 40C is feasible because key microorganisms, including *Dehalococcoides sp* (Dhc), can quickly recolonize in the subsurface. There may be a delay, but microorganisms can re-establish naturally although anaerobic destruction of chloroethenes normally occurs at temperatures above 50C.
- Thermal treatment may increase the levels of available carbon, stimulating subsequent dechlorination and reducing competition for electron donors.
- The combination of thermal treatment with chemical reduction approaches (such as emplaced zero-valent iron, ZVI) can increase the rates of contaminant recovery from slowly desorbing soil fractions.
- In Situ Chemical Oxidation (ISCO) after thermal temperatures have cooled to 50C is ideal for thermal activation of sodium persulfate.
- Initial results from combining heating with ISB and In Situ Chemical Reduction (ISCR) (ZVI injections) suggest both combinations can be economically beneficial.

**Best Practices for Thermal Implementation.** The three dominant (Figure 11) and most used technologies include:

- In Situ Thermal Desorption (ISTD),
- Electrical Resistance Heating (ERH), and
- Steam Enhanced Extraction (SEE).

ISTD and ERH work well in low-permeability formations. Steam injection relies on advection for delivery and is more appropriate for permeable formations with rapid groundwater flow. Combinations of ISTD or ERH with SEE have been used to effectively treat heterogeneous sites containing both high- and low-permeability media (Heron et al 2005).



**Figure 11 - Heating Patterns** Heron, G., S. Carroll and S. G. D. Nielsen. 2005. Full-Scale Removal of DNAPL Constituents using Steam Enhanced Extraction and Electrical Resistance Heating. *Ground Water Monitoring and Remediation* 25 (4), Fall, 92-107.

## Selecting the Best Technology for a Site – And Combining Technologies for Improved Performance .

A strong site understanding is crucial for selecting the best remedial actions for a site:

- The area that exceeds the remedial goals must be definitively determined, in both areal extent and depth. Data collected using HRSC techniques yield the most reliable results to limit the extent of treatment area and provide a cost-effective approach.
- A solid conceptual site model (CSM) must be developed such that the COC distribution, lithology and hydrogeology, and COC behavior are understood. Note these are dynamic documents that need to be continually updated during the site characterization and remediation process.
- Mass estimates are critical for determining feasibility of thermal and combined non-thermal approaches.

Remedies can be combined in two ways:

- Spatial treatment: One technology used to treat the source areas while another is used in the surrounding, less contaminated zones.
- Temporal treatment: A single technology is applied where appropriate, followed by a second technology for polishing to lower concentrations.

One example of spatially-combined remedies is depicted in Figure 12. A thermal remedy is applied in the source area, and a reactive barrier of ZVI is placed around the thermal treatment area to degrade TCE that is produced when steam is generated in the source area and to provide TCE containment. For the less contaminated distal areas, ISB in the form of enhanced reductive dechlorination can be used.

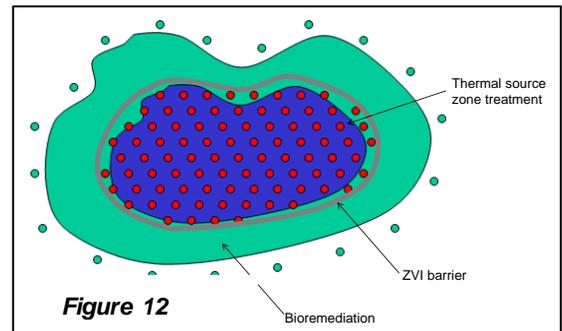


Figure 13 illustrates one temporal option for a combined remedy. A non-thermal technology such as ISB is first used to immediately shrink and control the dissolved plume. Performance monitoring data are used to determine progress, and towards the end of this phase additional site characterization is used to pin-point zones needing more aggressive treatment. In this way, the area and depth addressed by thermal technologies is minimized, along with the expense and resource needs.

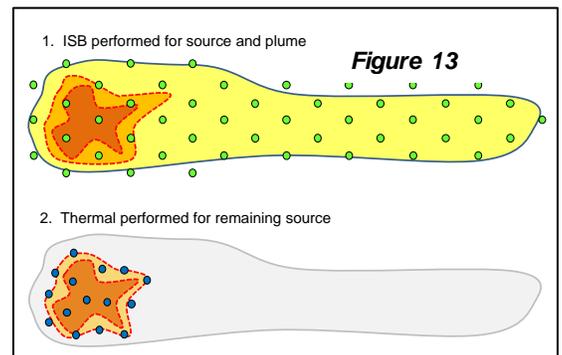
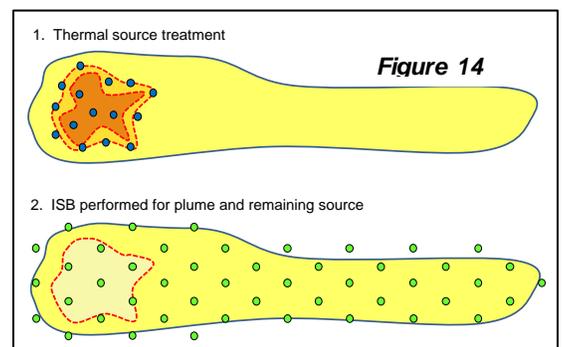


Figure 14 illustrates a second temporal combined remedy option, where the source area is treated first, followed by polishing of the surrounding areas (and any leftover COCs in the source) using non-thermal technology. This option is particularly attractive in that:

- Immediate NAPL spreading risks are eliminated,
- Vapor intrusion risks are strongly reduced by removal of the majority of the COC mass, and
- The non-thermal treatment approaches (such as ISB or monitored natural attenuation, MNA) have a better chance of meeting remediation goals in a timely manner when the mass discharge from the source is reduced.



Combining remedies is recommended:

- **When there is time:** Most combined remedies take longer than using thermal alone. If there is sufficient time to allow the non-thermal technologies to be effective, the area requiring thermal treatment can be limited.
- **When sites are complex:** Site complexities such as great depth, presence of bedrock, multiple layers with contrasting permeability, or simply thick clayey zones are challenging for the non-thermal technologies. Thermal treatment can be successful despite these complexities, and combining thermal with other remedy options for the less-challenging impacted areas improves cost-effectiveness.
- **When you have high amounts of mass:** Thermal treatment can address areas of high contaminant mass much more effectively, while non-thermal technologies are sufficient and more cost-effective in the less contaminated distal areas outside of the source zones.

While these examples have focused on combinations including thermal treatment, similar combinations are available for sites with less contamination. For instance, ISCO source reduction may be combined with ISB or MNA to treat both the source and plume.

**4.b. In Situ Chemical Oxidation (ISCO)** ISCO is injecting a massive supply of thermodynamically powerful electron acceptors into the subsurface. Commonly used substrates are permanganate, hydrogen peroxide, and activated sodium persulfate. ISCO is attractive because it provides rapid in situ destruction, but rebound and incomplete treatment have been consistent problems and ISCO can be only marginally effective on chloroethene source treatment.

Rebound has been attributed to:

- Reactants that are short-lived and thus do not reach contaminants in low permeability zones.
- Sorbed contaminants that may be released following oxidation of natural organic matter.
- Delivery challenges – where the reagent fails to come in contact with a substantial fraction of the mass.

Improvements in ISCO include development of stabilized Catalyzed Hydrogen Peroxide (CHP) and activated persulfate. Techniques have been developed to stabilize hydrogen peroxide through addition of organic acids (phytate), allowing the oxidant to persist longer and further downgradient of the injection location. Activated persulfate can treat a wide range of contaminants and is relatively stable and not as reactive with natural organic matter (NOM).

**Observations of ISCO Performance Prior to 2007 (the last published national data set).** Based on our experience implementing hundreds of ISCO designs and review of performance monitoring data, we believe the less-than-stellar performance degrading chlorinated solvents can be attributed to:

- DNAPL or Mass sorbed to soils was overlooked, and required multiple applications to liberate and treat.
- Hydraulics and kinetics were not considered in the radius of influence design estimates (e.g. injection volumes too low).
- Data derived from monitoring wells data were insufficient to defined target intervals.
- Injections were executed through wells in highly heterogeneous sites.
- Insufficient attention was paid to parameters such as distribution, pressure, flows, tooling, and approach (e.g., wells or disposable points, bottom-up versus top-down, fracturing, etc.).

ISCO source zone efforts can be combined with other technologies taking into consideration:

- The subsurface may be partially sterilized. Research examining the coupling of ISCO with bioremediation indicates that such impacts are generally minor.
- ISCO may improve subsequent ISB polishing treatment by increasing dissolved organic matter content.
- Permanganate treatment can favor Mn-reducing bacteria that use hydrogen to reduce MnO<sub>2</sub> precipitates thereby inhibiting later dechlorination.

One notable example of combining ISCO with other technologies is heat-activated persulfate, which can increase COC removal during thermal treatment by increasing the accessibility of contaminants as well as activation of the persulfate. These studies indicate that ISCO is compatible with other technologies and that secondary effects can be managed with careful design.

### **Moving Beyond Bench Scale Test Performance**

**Catalyzed Hydrogen Peroxide (CHP) Scale Up.** Field application design considerations include:

- CHP is sensitive to subsurface conditions and can decompose in minutes or persist for days. Stabilizing hydrogen peroxide can improve overall residence time.
- Low residence time challenges the ability to treat mass sorbed into the soil matrix.
- Gas and heat evolution limits injection concentration and can result in significant daylighting, impacting COC contact.
- The actual NOM demand is unquantifiable; dosing assumes an effective versus actual NOM demand, making it difficult to accurately dose.
- Injection concentration is often limited to less than 12 percent and about 5 percent effective pore volume achieving the desired radius of influence is heavily dependent on advective transport.

The success of CHP, is primarily focused on applying the technology to the right hydrogeological and soil conditions, considering low residence time, while other technologies have more flexibility with longer persistence and better distribution through advection and diffusion.

**Permanganate Scale Up.** Field application design considerations include:

- Closure monitoring typically cannot commence until the permanganate is spent, often delaying closure for years if site has been overdosed.
- It is generally difficult to maintain a soluble potassium permanganate solution at concentrations < 2.5 percent without aggressive mixing for extended timeframes or by heating the solution.

Slow dosing of permanganate to slowly overcome oxidant demand, increasing residence times, and avoiding overdosing resulting in monitoring delays has proven effective in a wide range of soil and hydrogeological conditions.

**Activated Sodium Persulfate Scale Up.** Field application design considerations include:

- Persulfate generates acid during decomposition; buffering of the injection solution with sodium hydroxide is required to activate the persulfate for its expected persistence of approximately 30 days. It can be difficult to maintain the pH within the target window of 10.5 to 12 without performing buffering tests on site soils.
- Peroxide and iron activation results in low pH conditions that are not compatible with carbon steel injection tooling. Therefore, distribution through monitoring wells is required.

Due to persulfates electrical conductivity (EC) response, distribution can be confirmed by EC logging to optimize contact with contaminants.

**Design Optimization Testing (DOT).**

Due to the high dependence on COC contact for ISCO success, DOT (formerly called pilot scale testing) is required to confirm site-specific distribution performance, injection design parameters (pressures, flows, tooling, ROI), and any potential injection issues like daylighting or surfacing (a risk with CHP). Typically, DOT monitoring is more extensive than full-scale performance monitoring which is primarily focused on only treatment efficacy and appropriate field parameters (determined based on DOT results).

**Overcoming Matrix Back Diffusion.**

Since ISCO is a relatively short-lived treatment technology, effective design assumptions, as outlined below, must address how to dose for mass in the sorbed or DNAPL phases that is not readily available for treatment unless in the dissolved phase. Therefore, unlike ISB or ISCR designs which have considerably longer persistence, the design best practices for ISCO should account for the eventual transition of mass bound up in soil and DNAPL to the dissolved phase and should not initially overdose by assuming this mass is all readily available for treatment. A typical dosing equation for determining oxidant dosing is presented on the following page. It is recommended to dose to treat all the dissolved phase plus a percentage of sorbed or DNAPL mass over multiple events. For example, twice the dissolved phase concentration can be targeted as a way to compensate for the dissolution of sorbed or DNAPL mass into the dissolved phase. To expedite DNAPL and sorbed mass treatment over equilibrium rates one can inject surfactants, heat the subsurface, or recirculate reagents to increase the residence time of the oxidants within the dissolved phase.

- $C_S$  = Contaminant Concentration in soil (mg/kg)
- $C_{GW}$  = Contaminant Concentration in groundwater (ug/l)
- $C_{NPL}$  = Contaminant Concentration in NAPL phase (mg/l)  $P_E$  = Effective Porosity
- $G$  = Gallons Water To Be Treated ( $X*Y*Z*P_E$ )
- $Y_S$  = Yards of Soil To Be Treated ( $X*Y*Z*(1-P_E)$ )
- **$S$  = Stoichiometric requirements per pound of contaminant**
- $S_R$  = Scavenging Reactions
- $C_F$  = Confidence Factor (*lithology, hydrogeology, characterization*)
- $T_R$  = Total Pounds of chemistry required**

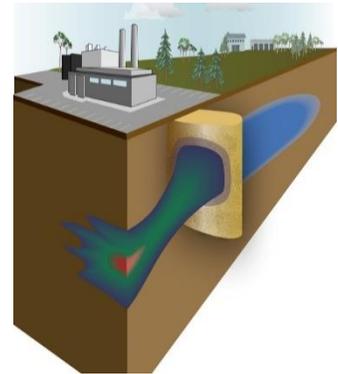
$$T_R = \{((C_{GW} * G) + C_{NPL} + (C_S * Y_S)) * S + (S_R)\} * C_F$$

Not Readily Available for Treatment  
Until They Transition to Dissolved Phase

**Figure 15 - Dosing for Mass Sorbed to Soil or in NAPL Phases**

**4.c. In Situ Chemical Reduction (ISCR)** ISCR is the transfer of electrons to contaminants from reduced metals (ZVI, ferrous iron) or reduced minerals (magnetite, pyrite, mackinawite, etc.).

A Permeable Reactive Barrier (PRB) remedy constructed using granular ZVI (“iron wall”) is an example of ISCR where the chemical reaction occurs on the surface of ZVI particles as impacted groundwater flows through the wall. Many types/forms of injectable ISCR products are also available, containing a more fine-grain ZVI (micro or nano), ferrous iron and/or reduced minerals. Advanced ISCR reagents take advantage of the fact that fermentation of organic carbon in proximity to iron or iron-bearing minerals increases both reactivity and longevity of the iron component (alkaline/acid balance). (Figure 16).



**Figure 16 - ISCR Permeable Barrier Application**

ISCR occurs naturally as Fe(II) minerals can degrade chlorinated ethenes without harmful intermediates, but this process has not been used widely for source treatment. Engineered ISCR using ZVI in PRBs is a proven plume treatment technology, but the microscale ZVI used for these barriers can be difficult to effectively distribute during injections and requires pneumatic or hydraulic emplacement technologies.

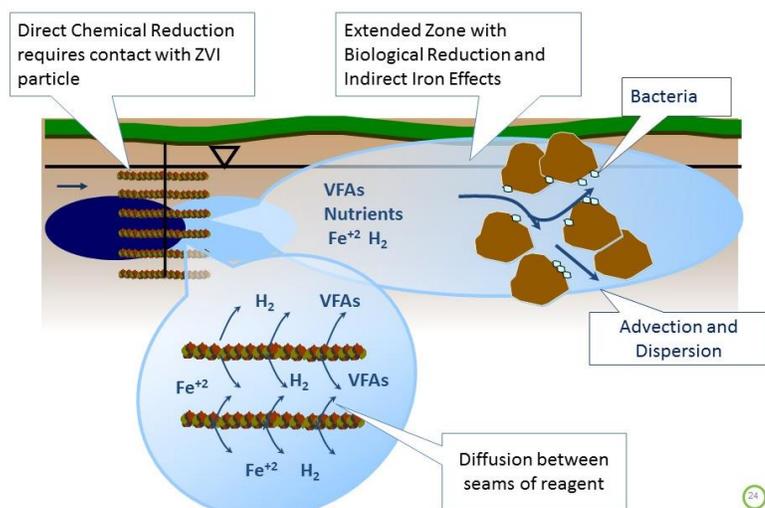
ISCR is rarely used to treat sources except in conjunction with ISB. The combination of ZVI (abiotic) with electron donors (biotic) offers the potential for rapid chemical degradation of the most accessible contaminants, combined with the longer-lasting bioremediation. The effects of ZVI on biochemistry and indigenous microbial populations appear minimal and may result in sustained reductions in oxidation reduction potential (ORP) that can enhance subsequent anaerobic biodegradation.

The dechlorination of TCE and PCE through ISCR results in less accumulation of metabolites (cis-DCE, VC) than enzymatic systems. The secondary dechlorination pathway can be biological and the tertiary dechlorination pathway can be indirect chemical reduction catalyzed by biogenically formed reduced iron and iron sulfide mineral (Figure 17.)

**Aspects of an Effective ISCR Strategy.** Solid (ZVI + fibrous organic carbon) ISCR reagents such as EHC<sup>®</sup> provide strong kinetics, multiple degradation pathways, longevity, and the ability to address back diffusion for source area treatment.

The advancement of including an organic carbon donor with micro-scale ZVI has expanded the range of ISCR applicability such that it can simultaneously treat metals, can be sequentially combined with ISCO, and facilitate post-treatment progression to MNA.

ISCR technology is flexible as a variety of ZVI, organic carbon substrates and related additives can be mixed to customize the reagent to site-specific requirements. The capabilities of biogenically formed iron and sulfide minerals are now well known.

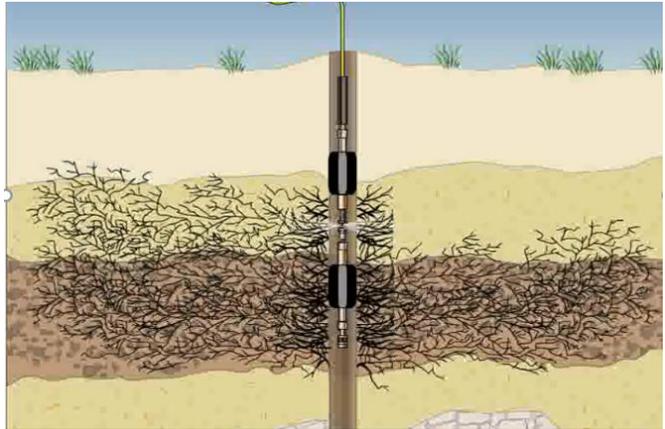


**Figure 17 – Biotic/Abiotic Reactions and Distribution Associated with ISCR**

**Full-Scale ISCR Considerations.** Developing an effective dosing rate to meet clean-up goals does not depend solely on the contaminant mass and quantity of competing electron acceptors. Since treatment of CVOCs in source areas often requires injection of large volumes of ISCR reagent, the challenge is how to inject and distribute these large volumes.

Consideration must be given to the relative mass/volume ratio between the reagent that is to be injected and the volume of soil and groundwater that can be physically influenced. Emplacement of the technology is critical to accomplishing required contact. For ISCR, pneumatic or hydraulic emplacement is required to ensure contact between the reagent and the impacted media (Figure 18). Dosing rates/volumes are optimized based on pump pressure versus flow rate capabilities. Best practices for pneumatic and hydraulic emplacement of ISCR reagents include the following guidelines:

- Emplace at greater than 10 feet below ground surface to minimize daylighting and enhance contact.
- Distribute reagent at high injection rates to maximize lateral distribution.
- Utilize multiple lines of evidence to verify distribution, (e.g., pressure monitoring wells, points of compliance wells, tilt meters).
- Stagger locations and vertical intervals and overlap areas of influence.
- Don't skip intervals or reallocate amendments.
- Use directional tools versus radial as needed for better targeting in desired directions.



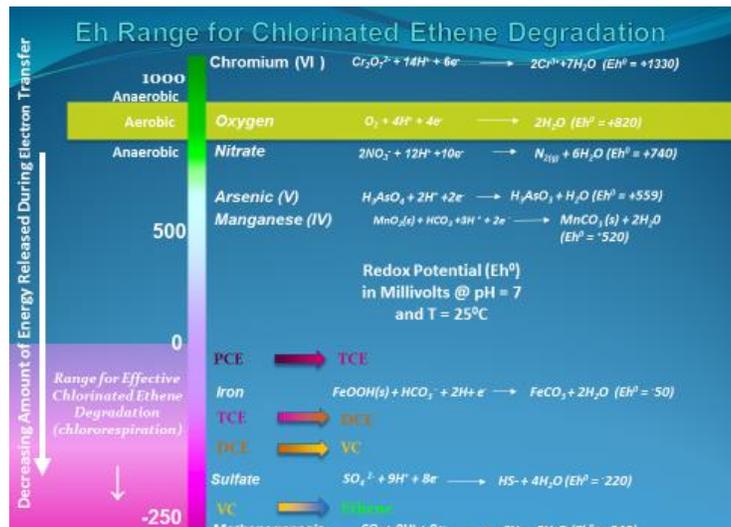
**Figure 18 - Pneumatic Emplacement Through Straddle Packers**

**4.d. In Situ Bioremediation (ISB).** Anaerobic biostimulation is the modification of the environment to stimulate existing bacteria capable of bioremediation of chlorinated solvents at low Eh levels (Figure 19). This occurs by adding the following to groundwater:

- Electron donors – e.g., lactate, EVO, lecithin, cellulose, lactose
- Nutrients – e.g. nitrogen, phosphorous, potassium

Bioaugmentation is the introduction of a group of natural microbial strains to achieve bioremediation

- Indigenous – native to site
- Exogenous - introduced



**Figure 19 - Eh Range for Chlorinated Ethene Degradation**

ISB is most appropriate for plume areas where COC concentrations tend to be more dilute (Figure 20). Key elements to consider when evaluating an ISB remedy include:

- **Flow regime.** It is typically difficult to maintain reducing conditions in high-flow settings, with the influx of groundwater with native electron acceptors (e.g. high dissolved oxygen).
- **Target formation lithology.** Injecting into tight formations with low flow conditions can be difficult, resulting in limited contact between substrate and groundwater. This situation can be mitigated through hydraulic or pneumatic emplacement.
- **Type and concentration of contamination.** ISB is appropriate to treat groundwater with total chlorinated ethane ranges from 0.01 to 100s of mg/L (though effectiveness decreases at higher and lower concentrations). ISB is effective for residual or sorbed DNAPL, but not appropriate for free product. Figure 19 identifies where ISB can be applied and expected orders of magnitude treatment.
- **Background sulfate concentrations.** Carbonate aquifers are typically high in sulfate concentrations. Sulfate reduction stimulated by anaerobic bioremediation produces hydrogen sulfide (HS), which is toxic to bacteria. If sufficient ferrous iron is not present in solution to bind the sulfide in a ferrous sulfide species, toxic levels of HS may accumulate and ISB will not be effective.

If not properly designed and implemented, ISB can cause undesirable side effects, notably pH decreases, methane generation, and increases in dissolved metals (especially iron and arsenic). These effects can persist for years but generally return to near baseline conditions within a short distance of the treatment area. Guidance is available to help understand these secondary impacts, and design appropriate loading rates to minimize these problems. Key design elements are discussed in the following sections.

**Substrate Selection.** Substrate selection is critical, since substrates do not release hydrogen at the same rate, are not transported through the aquifer at the same rates, and do not have the same electron donor capacity. Substrates are available in soluble and slow release forms, and can be combined both temporally and spatially. Factors to consider in substrate selection include:

- Contaminant distribution and hydrogeology
- Required persistence/longevity
- Delivery approach
- Size for distribution by advection
- Synergy with bioaugmentation cultures
- Impacts on groundwater pH

**Substrate Loading Rate.** The appropriate level of substrate must be distributed in the subsurface to develop optimal geochemical and redox conditions for anaerobic processes without creating adverse conditions. The goal is to achieve uniform distribution in 4 dimensions, space and time. The design factors include target demands, residence time, injection volume to achieve desired ROI, substrate concentration in the injection solution and

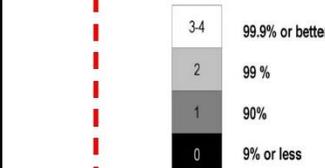
Phase / Zone	Source Zone		Plume	
	Low Permeability	Transmissive	Transmissive	Low Permeability
Vapor	0- Depletion of contaminants in the saturated zones is likely to have little effect on vapor phase contaminants			
DNAPL	0 - high concentration in DNAPL and the potential for limited biological activity 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 20– ISB Effectiveness in 14 Compartment Model

frequency of injections. Insufficient loading or distribution will not fully produce the required reducing conditions, resulting in the accumulation of intermediate degradation products.

Typical loading rates in the aquifer pore volume are between 1 to 10 g/L; greater than 10 g/L can be toxic for bioaugmentation. Excessive substrate will also result in:

- Uncontrolled fermentation reactions (producing ketones and methane)
- Lowering of pH to adverse level biologically activity (< 5.5)
- Degradation of secondary water quality parameters (e.g., mobilizing metals)

Substrate examples are included in Figure 21 below.

Substrate	Typical Delivery Technique	Form of Application	Injection Frequency
<b>Common Soluble Substrates</b>			
Lactate, lactic acid, butyrate	<ul style="list-style-type: none"> <li>• DPT Injection</li> <li>• Injection Wells</li> <li>• Circulation systems</li> </ul>	Diluted in water	Continuous over short periods to monthly
Molasses, high fructose corn syrup	<ul style="list-style-type: none"> <li>• Injection wells</li> <li>• Circulation systems</li> </ul>	Dissolved in water	Continuous over short periods to monthly
<b>Common Slow Release Substances</b>			
Vegetable oil emulsions	<ul style="list-style-type: none"> <li>• Direct injection</li> <li>• Injection wells</li> </ul>	Low oil content (<10%) microemulsions suspended in water	Every 2-3 years (typically); one-time application possible
Whey	<ul style="list-style-type: none"> <li>• Direct injection</li> <li>• Injection wells</li> </ul>	Dry or dissolved in water or slurry; dry product more commonly used	Monthly to yearly
Lecithin emulsion	<ul style="list-style-type: none"> <li>• Direct injection</li> <li>• Injection wells</li> </ul>	<20% lecithin microemulsions suspended in water	Every 2-5 years; one-time application possible

**Figure 21 – Substrate Examples**

**Substrate Delivery.** The goal is to achieve effective contact between the reagents and the COCs. Various delivery approaches for consideration include direct targeted injection (borings, DPT tools); pneumatic or hydraulic emplacement, injection wells, and recirculation systems. Factors to be considered when designing the distribution approach include:

- Injection frequency
- Injection volume (e.g., full pore volume replacement)
- Injection sequence (outward-in, top-down, bottom-up, alternating)
- Estimated distribution radius (ROI, spacing between points and between rows)
- Residence time within the treatment zone taking into account matrix back diffusion rates

**Dilution/Chase Water.** The best practice is to use conditioned treatment-area groundwater for substrate dilution or chase water. Groundwater should be extracted, conditioned to a strongly reducing state, and blended with substrate and a bioaugmentation culture in a batch tank. This approach:

- Minimizes plume displacement,
- Maintains treatment zone geochemistry,
- Utilizes indigenous microbial cultures to condition water, and

- Quickly establishes optimal conditions in the target aquifer to rapidly develop robust dechlorinating microbial culture.

Site Groundwater can be conditioned to a strongly reducing state with:

- Sodium lactate (easy to use, quick release donor, easy tank cleaning, relatively inexpensive),
- Emulsified vegetable oil (slow release, do not put in tanks due to difficult cleaning),
- EHC/ZVI, or
- Sodium sulfite.

While hydrant water is easier to obtain than groundwater, especially from formation with low extraction rates, it is less than optimal since it:

- Requires more effort to condition to strongly reducing state biologically,
- Contains oxygen, and
- Contains chlorine/chloramines to kill bacteria, which may slow the process for rapidly developing robust dechlorinating microbial culture.

**Bioaugmentation.** Only one organism (*Dehalococcoides sp - Dhc*) will completely degrade PCE and TCE to non-toxic ethane. Determining the population of indigenous Dhc is extremely difficult and expensive. Dechlorinating organisms may not be present at sufficient concentrations at many sites, since greater than  $1 \times 10^7$  Dhc cells/L are considered necessary for remediation. Additionally, the indigenous Dhc organism may not be efficient at dechlorination and the final step may be co-metabolic, which is slow.

Dhc dechlorination rates are directly related to pH (Figure 22), with the optimal target range from 5.5 to 8.5. pH reductions as a result of treatment can be mitigated by:

- Pre-screening the site buffering capacity (red flag = pH < 6 and alkalinity < 300 mg/L).
- Modifying the substrate mixture and loading rate (e.g. less concentrated, more frequent injections).
- Using a buffered substrate or adding buffering agent to injection solution, such as sodium bicarbonate, potassium bicarbonate, sodium hydroxide, or calcium carbonate. Additionally, care is needed when adding buffer to bioaugmented delivery water since it may raise the pH too high for the Dhc.

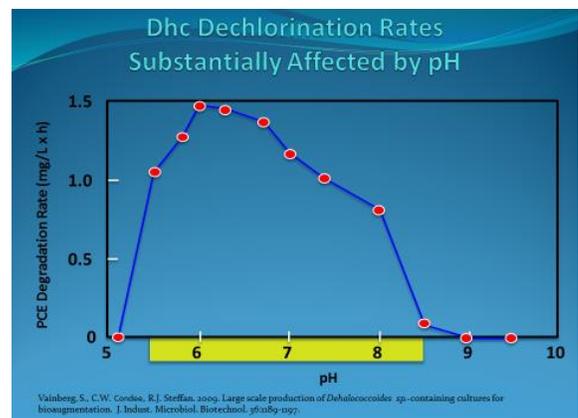


Figure 22- Dhc degradation rate (PCE) versus pH

**Performance Monitoring.** Wells within, upgradient, and downgradient of the treatment area should be monitored for performance. Monitoring parameters are focused on substrate delivery and remedy effectiveness, and include:

- Substrate persistence/longevity including soluble total organic carbon,
- VOC concentrations,
- Dissolved gases (ethene, ethane, methane),
- Dissolved metals (Mn, As, Fe),
- Anions (nitrate and sulfate), and
- Water quality parameters (dissolved oxygen, ORP, pH, temperature, specific conductivity, turbidity).

**4.e. Monitored Natural Attenuation (MNA)** MNA is a remediation process that includes a variety of physical, chemical, or biological processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or groundwater. As depicted in Figure 2, a remedy change should be considered after successfully mitigating any vapor intrusion risks, and either achieving MCLs or reaching asymptotic COC recovery. A transition assessment and proposal is made to regulators to support

a longer-term passive or active management strategy and ultimately achieve unlimited use and unrestricted exposure for the site.

During passive or active long-term management, MNA is a commonly accepted approach to managing plumes from chlorinated solvent source zones. In a study (NRC, 2013) of 191 sites, MNA was:

- the sole remedy at 30% of the sites;
- used in conjunction with some type of active treatment at 47% of the sites; and
- was determined infeasible at 23% of the sites.

Sixteen of the sites where MNA was used as a remedy had maximum concentrations greater than 10 mg/L and a median groundwater seepage velocity of about 50 ft/yr. Key reasons rejecting MNA as a remedy included expanding plumes and/or unreasonably long projected cleanup time frames. Biodegradation was reported to be the most important MNA process at 70% of the sites.

The success of natural attenuation as a remedy depends on the site-specific ability to predict the evolution of complex biogeochemical processes over an extended period of time. Because of uncertainties in long-term predictions, natural attenuation requires confirmation through a detailed monitoring program. The need for a contingency plan is important to provide a cleanup approach that will be implemented if MNA fails to perform as anticipated. This plan could include optimization of source or plume treatments, implementation of an enhanced attenuation technology, or institutional controls. MNA systems could fail for many reasons, such as temporal changes in site specific hydrogeologic and geochemical conditions, depletion of natural sources of nutrients or electron acceptors/donors, or lower-than-anticipated transformation rates.

A properly designed monitoring program should provide early detection that allows the implementation of a contingency plan prior to the point when a migrating plume would present elevated risks to receptors. If contaminant migration and/or plume expansion occurs prior to the detection of a failure, additional costs will be incurred and the combined cost of the failed MNA and an additional remedy could exceed the cost that would have incurred had a more active remedy originally been implemented. For sites where contamination remains in place, an evaluation of the potential events (e.g., floods, earthquakes, sea level rise, etc.) that could lead to failure of the long-term management approach should be performed and contingency plans developed. In addition to MNA, long-term management typically includes institutional controls.

**4.f. Long-Term Management - Institutional Controls (ICs).** ICs are administrative and/or legal controls that minimize the potential for human exposure to contamination and/or protect the integrity of the remedy, generally by attempting to modify human behavior. For example, property controls are a private agreement between the current property owner and regulatory agency that define use restrictions, for example a restrictive covenant prohibiting the extraction of groundwater for drinking water on a property with impacted groundwater. Direct government controls, zoning laws, and building codes can also be used. ICs are recorded in property records and provide advisories as required by regulatory decision documents. Although not enforceable, they may be required by an enforceable consent decree or other instruments. ICs may restrict future economic development, though enforcement is not clearly defined.

Note that the USEPA does not pay for monitoring and enforcing ICs because statute requires states to ensure payment for all future routine operations and monitoring following CERCLA-financed remedial actions. However, where private companies or other federal agencies perform the cleanup, they and not the states pay for monitoring and enforcing the ICs.

ICs have failed for a number of reasons:

- They rely heavily on humans to implement, oversee and administer.
- Monitoring and maintaining an IC is a low-priority, especially when the purpose is not readily apparent and indeed is often buried underground.
- Zoning requirements can be modified by political bodies.
- Regulators may not be able to enforce restriction on subsequent property owners.
- The USEPA doesn't regularly consult with local authorities.
- ICs may not be implementable by local government.

However, the USEPA has substantially improved the process for developing, implementing and enforcing institutional controls.

Institutional controls, maintenance and enforcement costs may extend beyond the 30-year period traditionally used in many response cost calculations. The USEPA now recommends direct payment from responsible parties, settling party trust funds, surety bonds, letter of credit, or insurance to fund site specific accounts for ICs.

The primary risk from failure to establish or enforce an adequate set of ICs is that the public may be exposed unknowingly to contaminated groundwater or vapor intrusion at levels above those allowing unlimited use and unrestricted exposure. This exposure could lead to property damage or personal injury lawsuits and undermines the credibility of regulators and local officials with the public, which is likely to make long-term management of the site more difficult and more expensive.

## **5. Conclusions**

We understand that there a multitude of competing factors when deciding how aggressive one needs to be in cleaning up chlorinated solvent sites. The competing factors fall under what we call "drivers," which can include; risk minimization, litigation, compliance, performance based contracts, and property transfer which all balance against the responsible party's ability to fund the remediation. This makes our RORI approach a critical component of any remediation strategy to effectively manage long-term life cycle costs.

Over the past 20 years, Cascade has actively been characterizing and remediating chlorinated solvent sites across the country. During this time, we have developed a field-proven knowledge base as to what works in terms of design principles and implementation best practices and what doesn't work in terms of the limitations to site characterization and remediation technologies. Within the industry, we are now poised for improved performance and reducing the number of the sites that pose risks to our communities.

We advocate the use of best design and implementation practices from site characterization, through remediation, and ultimately to long-term management to achieve MCLs for unrestricted exposure and unlimited use. With advances in HRSC and remediation technologies, attractive RORI's are more achievable than ever. Some these advances include:

1. MiHPT and 3D imaged remediation designs
2. Waterloo<sup>APS</sup>
3. Thermal and ISB, ISCO, or ISCR combined remedies
4. Abiotic and biotic remediation combined remedies
5. ISCO with ISCR and ISB combined remedies
6. ISB with Bioaugmentation
7. Hydraulic and pneumatic emplacement for ISB, ISCO, and ISCR remedies

The next few years should be dynamic as regulatory agencies decide how best to regulate and respond the acute short-term risks of TCE.

## 6. Reference Documents



Home > Tools and Training > Environmental Restoration > DNAPL Source Zones > Chlorinated Solvents On-Dem...

Tools for Management of Chlorinated Solvent-Contaminated Sites

Type: On Demand Video

Chlorinated Solvents On-Demand Video

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

July 2008

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

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### Chlorinated Ethene Source Remediation: Lessons Learned

Hans F. Stroo,<sup>1,\*</sup> Andrea Leeson,<sup>2</sup> Jeffrey A. Marqusee,<sup>3</sup> Paul C. Johnson,<sup>4</sup> C. Herb W. Michael C. Kavanaugh,<sup>2</sup> Tom C. Sale,<sup>5</sup> Charles J. Newell,<sup>6</sup> Kurt D. Pennell,<sup>7</sup> Carme and Marvin Unger



Technical/Regulatory Guidance

#### In Situ Bioremediation of Chlorinated Ethene: DNAPL Source Zones



**FINAL**

**Principles and Practices of Enhanced Anaerobic Bioremediation of Chlorinated Solvents**



August 2004



#### ADDENDUM TO THE PRINCIPLES AND PRACTICES MANUAL

Loading Rates and Impacts of Substrate Delivery for Enhanced Anaerobic Bioremediation

ESTCP Project ER-200627

JANUARY 2010

Shawn Healy  
Parsons Infrastructure & Technology Group, Inc.



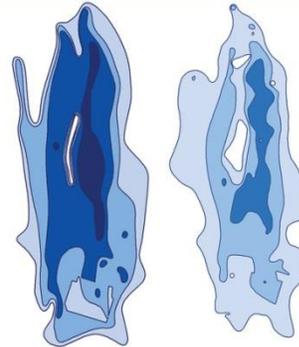
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## In Situ Chemical Oxidation for Groundwater Remediation

R. L. Siegrist  
M. Crimi  
T. J. Simpson  
Editors

NATIONAL RESEARCH COUNCIL OF THE NATIONAL ACADEMIES

### ALTERNATIVES FOR MANAGING THE NATION'S COMPLEX CONTAMINATED GROUNDWATER SITES



### Study and Interpretation of the Chemical Characteristics of Natural Water

Third Edition

United States Geological Survey  
Water-Supply Paper 2254



Engineering Issue

#### In-Situ Chemical Oxidation

Scott G. Huling<sup>1</sup> and Bruce E. Pritzl<sup>2</sup>

##### I. PURPOSE

The U.S. Environmental Protection Agency (EPA) Engineering Issue Papers are a series of technology transfer documents that summarize the latest available information on specific technical issues, including fate and transport, specific contaminants, selected treatment and site remediation technologies, and related other issues. This Engineering Issue Paper is intended to provide remedial project managers (RPMs), on-scene coordinators (OSCs), contractors, and other state, industry, or private remediation managers with information to assist in the evaluation and possible selection of appropriate in-situ chemical oxidation (ISCO) remedial alternatives.

This Engineering Issue Paper provides an up-to-date overview of ISCO remediation technology and fundamentals, and is developed based on peer-reviewed literature, EPA reports, web sources, current research, conference proceedings, and other pertinent information.

##### II. INTRODUCTION

###### A. Background

In-situ chemical oxidation involves the introduction of a chemical oxidant into the subsurface for the purpose of transforming groundwater or soil contaminants into less harmful chemical species. There are several different forms of oxidants that have been used for ISCO; however, the focus of this Engineering Issue Paper will be on the four most commonly used oxidants: permanganate (MnO<sub>4</sub><sup>-</sup>), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and iron (Fe) (Fenton's reagent), or H<sub>2</sub>O<sub>2</sub>-derived oxidant, persulfate (S<sub>2</sub>O<sub>8</sub><sup>2-</sup>), and ozone (O<sub>3</sub>) (Table 1). The type and physical form of the oxidant influences the general materials handling and injection requirements. The placement of the oxidant in the subsurface is important since this affects the contact time for advective and diffusive transport and ultimately the delivery of oxidant to targeted zones in the subsurface. For example, permeable media for long periods of time, and diffusion into low-permeability materials and greater transport distances through porous media are possible. H<sub>2</sub>O<sub>2</sub> has been reported to persist in soil and aquifer material for minutes to hours, and the diffusive and advective transport distances will be relatively limited. Radical intermediates formed using some oxidants (H<sub>2</sub>O<sub>2</sub>, S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, O<sub>3</sub>) that are highly responsible for various contaminant transformations react very quickly and persist for very short periods of time (i.e., sec).

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