

Figure 1-1 Integrated DNAPL Remediation Decision-making

This chapter provides a framework for developing an adaptive strategy to select and integrate remedial options based on performance and compatibility. Fundamentally, the goal of applying one or more treatment technologies, in series or parallel, is to achieve the absolute objectives as quickly and efficiently as possible. From a more practical viewpoint, the goal is to apply treatment technologies to achieve SMART functional objectives, such as those described in [Table 3-3](#).

Treatment technology selection requires evaluating a number of different factors, including technical site considerations (e.g., geology, hydrogeology, and contaminants), regulatory requirements, sustainability and community stakeholder interests. Traditionally, treatment technologies are applied individually at a site, with the expectation that one technology will achieve both functional and absolute objectives. Recently, more comprehensive approaches have gained favor where site managers integrate multiple technologies, in both time and space, to meet functional and absolute objectives more efficiently, as in the Kings Bay site ([Text Box 4-1](#)) and Pemaco case studies (Appendix A).

2 and 3 to illustrate an approach of selecting and refining technologies in an IDSS remedy.

Text Box 4-1. Kings Bay, Coupling Technologies (see Appendix A)

The Kings Bay site was naturally anaerobic. A P&T system intended to contain the groundwater plume at the site boundary was not fully capturing the plume, and modeling indicated that, if plume concentrations were lowered to 100 µg/L total chlorinated VOCs, MNA would address the remaining contaminants before crossing the base boundary. Four injections of Fenton's reagent were conducted 1998–2001. ISCO reduced VOC levels to the target but made the aquifer aerobic in injection areas and some distance downgradient. Injections of emulsified vegetable oil returned the aquifer to anaerobic conditions. By 2004, VOC concentrations were reduced to <14 µg/L, and MCLs were met at the property boundary.

4.1 General Technologies Categories

Many technologies exist for chlorinated-solvent site remediation. It is useful to categorize available technologies according to the primary mechanism by which they impact individual chlorinated solvent phases (e.g., DNAPL, sorbed, dissolved, and vapor phases). For this document, the categories used are physical removal technologies, chemical/biological technologies, and containment technologies. [Table 4-1](#) identifies the technologies assigned to each category although it is also important to note that some technologies may be reasonably placed in more than one category.

Table 4-1. Technology categories

Technology category	Example technologies	Example references
Physical removal	Excavation	NAVFAC 2007
	Multiphase extraction	USACE 1999a
	Thermal conductivity/ electrical resistance heating	Johnson, Tratnyek, and Johnson 2009
Chemical/biological	In situ chemical oxidation	ITRC 2005b
	In situ chemical reduction	Liang et al. 2010
	In situ bioremediation	ITRC 2008b
	Monitored natural attenuation	ITRC 2008a
Containment	P&T	USEPA 1999
	Low-permeability barrier walls	NRC 1997
	Permeable reactive barriers	ITRC 2005a, 2011c
	Solidification/stabilization	USEPA 2009a, ITRC 2011a

[Table 4-1](#) is not intended as an exhaustive list of all technologies available. Those included have been successfully implemented for many years and at multiple sites. Other recent summaries (e.g., [Sale and Newell 2011](#), [Stroo and Ward 2010](#)) provide greater detail on these and other technologies. The following discussions focus on frequency of use, anticipated performance, and other considerations that are relevant for integrating remedies.

4.1.1 Considerations Regarding Technology Performance Assessments

Performance assessments using remediation results from multiple sites can provide general information regarding treatment effectiveness. For example, performance assessments at multiple sites have been conducted for a number of different technologies, including ISCO, thermal remediation, and bioremediation ([Geosyntec Consultants 2004](#); [McGuire, McDade, and Newell 2006](#); [Kingston, Dahlen, and Johnson 2010](#); [Krembs et al. 2010](#); [Lebrón, Major, and Kueper 2008](#)). An extensive 235 site database developed by ESTCP was published in 2016 ([McGuire et al., 2016](#)).

Some remediation professionals point to the following potential strengths associated with multisite remediation performance studies:

- Several studies report results by independent researchers in the peer-reviewed literature, which increases the level of confidence in the
- The performance studies are the only place where detailed before and after data have been made at multiple
- Some of the performance studies are able to compare different technologies using a repeatable, consistent
- Detailed information about how the technologies are applied is provided in several of the studies.
- The performance data represent what actually happened at a large number of sites, with results presented as a range, so the data likely describe a spectrum of sites. These sites range from sites with poor implementation practices and marginal site conditions to sites with good implementation practices and favorable site

However, other remediation professionals recommend caution when using results from multisite performance assessments and assessment comparisons between technologies for the following reasons:

- Assessments are based on literature reviews and/or surveys and represent the full spectrum of sites represented in those sources.

- The data from individual sites incorporated into the datasets are generally not evaluated or filtered for site-specific conditions that affect technology performance and that may also be difficult to quantify or are subjective, such as application to inappropriate sites, inadequate site characterization (e.g., source not fully defined), deficient design, or poor implementation by inexperienced practitioners).
- Data sets may lump pilot- and full-scale applications, for which the performance might be different.
- Finally, performance assessments do not factor in remediation objectives. For example, if a treatment objective is reached (e.g., 95% reduction), then a remediation is terminated even if greater reductions could be achieved by operating the remedy for a longer period of time.

Assessments of the frequency and magnitude of rebound must also be qualified due to similar problems. For example, the multisite remediation performance studies note rebound associated with chemical oxidation projects ([Geosyntec Consultants 2004](#); [McGuire, McDade, and Newell 2006](#); [Krembs et al. 2010](#)) but little or no apparent rebound observed with other remediation technologies ([Geosyntec Consultants 2004](#); [McGuire, McDade, and Newell 2006](#); [Kingston, Dahlen, and Johnson 2010](#)); however, such rebound assessments should consider treatment time frame. For example, McGuire, McDade, and Newell ([2006](#)) compared frequency of rebound at sites with at least 1 year of post-treatment data for ISCO, thermal remediation, and bioremediation but did not account for differences in treatment lifetime. For example, in situ chemical oxidants are typically consumed in days or weeks, while in contrast hydrogen production from bioremediation substrates are typically sustained for several months or even years after injection; thus, treatment from bioremediation substrates may still be occurring when rebound is assessed. Adamson et al. ([2010](#)) present a more detailed discussion of remediation time scales.

As mentioned above, the stages between technology selection and results monitoring (i.e., system engineering, construction, and operation) are rarely discussed even though their execution has great impact on project success, particularly in situ. The most important factor determining in situ project success is contact of reagent or energy with the targeted contaminated volume before it is consumed or degraded. A poor design precludes project success. Unfortunately, it is difficult to evaluate system design and whether its operation was optimized to determine its role in the ultimate outcome from a project history or summary of multiple sites addressed by a single remedial method. Therefore, published performance data, particularly for sites at which remediation began 10 or more years ago when techniques were less advanced, should be evaluated carefully during remedial method selection and system design and operation to determine its present applicability.

The following sections provide general summaries of remediation technologies in each of the technology categories and include data from multisite performance studies as percent reduction in source-zone concentration. Median values are reported both as percent contaminant reduction and the number of orders of magnitude (see Figure 1-1) reduction that were observed. There are five categories of orders-of-magnitude reductions:

- 9% reduction in concentration represents 3 OoM reduction in concentration
- 99% reduction in concentration represents 2 OoM reduction in concentration
- 90% reduction in concentration represents 1 OoM reduction in concentration
- 70% reduction in concentration represents 0.5 OoM reduction in concentration
- 10% reduction in concentration represents <0.1 OoM reduction in concentration

Orders-of-magnitude reduction can be calculated from contaminant percent reduction as follows: $\text{OoM} = -\log[1 - (\% \text{ reduction} \div 100)]$

4.1.2 Physical Removal Technologies

Physical removal technologies recover contaminants from the source location and subsurface. These technologies range from direct physical removal methods, such as excavation, to indirect removal methods, such as multiphase extraction (MPE) and thermal treatment, which are based on the physical properties of the contaminant (e.g., volatility, solubility, density, viscosity, or boiling point).

4.1.2.1 Excavation

Contaminants in the source zone are removed by excavation. The excavated material then is treated or managed, for example by on-site treatment or off-site disposal. Excavation is very effective for mass removal from near-surface source zones contaminated by strongly sorbed and/ or essentially immobile organic liquids (e.g., high-viscosity coal tars) and for recent release sites. This technology does not directly address aqueous- or vapor-phase contaminants, although source removal may reduce the mass and/or mass flux in those phases. Excavation is not used for plume areas due to the relatively

low contaminant mass in those compartments. Excavation becomes prohibitively costly with depth, and the carbon footprint associated with off-site hauling affects sustainability considerations.

Excavation was applied at 11 of 118 sites (9%) in a survey of DNAPL source zone treatment results ([Geosyntec Consultants 2004](#)). Ex situ source treatment technologies for which excavation is necessary as part of implementation (e.g., composting, off-site incineration, etc.) was a component of 104 of 230 (45%) source treatment decision documents at Superfund sites from fiscal years 2005–2008 ([USEPA n.d.](#)) although not all of these sites contained DNAPL (DNAPL sites were not separately identified in the Superfund Remedy Report data).

Relatively little multisite performance data for excavation were identified. DNAPL mass removal of 80%–100% (in the range of 0.7 or greater OoMs) was reported for three sites in a survey by Geosyntec Consultants ([2004](#)). Under ideal implementation conditions, contaminant mass removal is complete. However, in practice it is not uncommon for mass removal to be incomplete, and there are many circumstances in which the entire source area is not accessible for excavation (e.g., near a building, in bedrock, etc.).

4.1.2.2 Multiphase extraction

MPE combines groundwater P&T with SVE. Pumping extracts contaminated groundwater and draws the water table down to facilitate volatilization and removal of DNAPL and sorbed-phase chlorinated solvents through SVE. This approach can effectively remove all contaminant phases but becomes more costly and difficult with increasing depth and extremely high or low aquifer permeability. MPE preferentially removes contaminants from high-permeability intervals and has the potential to leave contaminant mass in lower-permeability intervals, depending on total time of operation.

MPE was applied at 13 of 118 sites (11%) in a survey of DNAPL source zone treatment results ([Geosyntec Consultants 2004](#)). MPE was a component of 12 of 230 (5%) source treatment decision documents and 1 out of 627 groundwater plume treatment decision documents at Superfund sites from fiscal years 2005–2008 ([USEPA n.d.](#)) although not all of these sites contain DNAPL (DNAPL sites were not separately identified in the Superfund remedy data).

Multisite performance data for MPE at DNAPL sites were not identified. Based on team experience, MPE is expected to be more effective on light, nonaqueous-phase liquid (LNAPL) than on DNAPL, and a reduction in source area contaminant concentration or mass by about 1 OoM is a reasonable expectation for a well-designed and effective system at an appropriate site.

4.1.2.3 Thermal conductivity and electrical resistance heating

Thermal technologies are included in the physical removal category because the primary removal mechanism is volatilization coupled with vapor extraction; however, other mechanisms, such as pyrolysis and hydrolysis, can destroy contaminant mass in situ if the soil is heated sufficiently. Two of the main thermal technologies used in IDSS applications are thermal conduction heating (TCH) and electrical resistance heating (ERH), with steam treatment being used less frequently. TCH technology uses heating elements in direct contact with the soil, resulting in heat transfer to the matrix. ERH technology applies electrical energy among electrodes, and the electrical resistance of the matrix to the flow of the electricity results in heating the formation. Thermal technologies are more demonstrated compared with other technologies for treatment of low-permeability media and for time-critical remediation ([NRC 2005](#)).

Thermal treatment can be applied sequentially or simultaneously with other technologies. For example, thermal treatment may be used to activate persulfate reagents during ISCO; however, maximum temperatures associated with thermal remediation inhibit the activity of some microbes while increasing the activity of others. Reductive dechlorination may also increase relative to pretreatment levels due to increased dissolved organic carbon concentrations and temperatures conducive to microbial activity ([Friis, Albrechtsen, and Bjerg 2005](#); [Friis 2006](#); [ITRC 2008b](#); [Pennell et al. 2009](#)).

Thermal technologies were applied at 27 of 118 sites (23%) in a survey of DNAPL source zone treatment results ([Geosyntec Consultants 2004](#)). Thermal technologies were a component of 12 of 230 (5%) source treatment decision documents at Superfund sites from fiscal years 2005–2008 ([USEPA n.d.](#)) although not all of these sites contain DNAPL (DNAPL sites were not separately identified in the Superfund remedy data).

Three multisite studies document the performance of thermal projects. McGuire, McDade, and Newell ([2006](#)) compiled performance data from three steam projects and three ERH projects and found that maximum source concentrations of “parent compounds” were reduced by 56%–99.96% with a median of 97% (equal to 1.5 OoMs) (insufficient data were available to evaluate total chlorinated VOC concentrations). Respondents to a survey by Geosyntec Consultants ([2004](#)) indicated data were available to assess mass removal for five thermal sites, for which mass removal was identified as 100%

for two sites, greater than 90% for one site, 50%–80% for one site, and 10%–25% for one site. Kingston, Dahlen, and Johnson (2010) evaluated post-treatment performance from 14 thermal treatments and found the treatment zone dissolved-phase concentrations were reduced by 1 OoM (90%) or less for nine of the sites, reduction was 1–2 OoMs for one site and ≥ 2 OoMs (99%) for four sites. The mass flux reduction was estimated to be ≤ 1 OoM at nine of the sites and ≥ 2 OoMs at the six of the sites (one site was counted twice, reflecting different vertical treatment intervals).

4.1.3 Chemical and Biological

Chemical and biological remediation technologies have been successfully used in IDSS applications. With chemical and biological technologies, contaminants are destroyed in situ through chemically mediated oxidation and or reduction or biological reactions.

4.1.3.1 *In situ chemical oxidation*

ISCO is the injection of oxidant and amendment solutions into the source zone and/or downgradient plume to destroy contaminants, primarily through chemical reactions. Oxidants include catalyzed hydrogen peroxide (Fenton's reagent or modified Fenton's reagent), ozone, permanganate, and persulfate. The oxidants react with the contaminants to produce nonhazardous intermediate and final products, such as carbon dioxide, carboxylic acids, and chloride from organic compounds, as well as iron, sulfate, and other ions from the catalyst amendments or the oxidants which may remain dissolved in groundwater or precipitate or react further with naturally occurring constituents of the soil or groundwater.

The wide range of options for ISCO and sensitivity to site conditions lead to complexity in design and application but also provide a wide range of applications. More than one application of ISCO is commonly performed at a site. ISCO can be applied over a wide range of concentrations to address dissolved, soil-sorbed, and DNAPL phases. However, different oxidants have different ranges of applicability. For example, catalyzed hydrogen peroxide is generally most applicable at higher concentration ranges and for DNAPL, while permanganate and ozone are generally more applicable at the lower concentrations found in dissolved plumes. Radical-based oxidants such as ozone, catalyzed hydrogen peroxide, and activated persulfate are applicable to a wide range of contaminants, including mono- and polynuclear aromatic

Text Box 4-2. Pall Aeropower, Rebound from Desorption (see Appendix A)

ISCO was able to destroy DNAPL and reduce dissolved contaminant concentrations to a greater degree than reductive dechlorination in the short term. However, desorption of soil-adsorbed CVOCs caused contaminant concentrations to rebound after the oxidants were consumed.

compounds, saturated (ethane) and unsaturated (ethene) chlorinated aliphatics, while permanganate is applicable to unsaturated chlorinated aliphatics and certain other compounds, such as phenols. The overlapping application range of different ISCO reagents also allows simultaneous or sequential application of different oxidants. For example, catalyzed hydrogen peroxide applied to destroy DNAPL at a site may be followed by permanganate, which is more persistent and destroys chlorinated solvents slowly desorbing from the soil and diffuses into fine-grained lithologic units (see [Text Box 4-2](#)). Hydrogen peroxide also catalyzes persulfate to produce oxidizing radicals, resulting in ISCO due to both catalyzed hydrogen peroxide and activated persulfate.

ISCO was applied at 25 of 118 sites (21%) in a survey of DNAPL source zone treatment results ([Geosyntec Consultants 2004](#)), at which permanganate was used for 15 sites (60% of the ISCO sites), catalyzed hydrogen peroxide for nine sites (36% of the ISCO sites), and ozone at one site (4% of the ISCO sites). ISCO was a component of nine (4%) out of 230 source treatment and 36 (6%) out of 627 groundwater plume treatment decision documents at Superfund sites from fiscal years 2005–2008 ([USEPA n.d.](#)), although not all of these sites contain DNAPL (DNAPL sites were not separately identified in the Superfund remedy data).

McGuire, McDade, and Newell (2006) compiled performance data from 23 sites containing DNAPL treated with permanganate (10 sites), catalyzed peroxide (8 sites), ozone (1 site), and combinations of oxidants (4 sites). The resulting data indicated a median reduction of 72% (0.6 OoMs) with a range of 10%–100% for total chlorinated volatile organic compounds (CVOC) concentration and a median reduction of 88% (0.9 OoMs) with a range from –55% (indicating a 55% increase in post-treatment concentration relative to pretreatment concentration) to 99.9% in “parent” compound concentrations. Respondents to a survey by Geosyntec Consultants (2004) indicated data were available to assess mass removal for 8 ISCO sites, for which mass removal was identified as 100% for 1 site, >90% (1 OoM) for 3 sites, 80%–90% for 2 sites, 50%–80% for 1 site, and 25%–50% for 1 site. Krembs (2008) and Krembs et al. (2010) compiled performance data from

242 ISCO projects. Their results showed a median reduction in treatment zone total VOC mass of 84% (0.8 OoMs) (ranging 73%–94%, 9 sites with data), and a median reduction in treatment zone maximum total CVOC groundwater concentration of 54% (0.3 OoMs) (ranging –146% [indicating an increase in groundwater concentration] to 99.7%, 55 sites with data); however, performance was also found to be correlated with oxidant type, contaminant type, geologic conditions, design criteria, and other factors.

McGuire, McDade, and Newell (2006) performed a detailed analysis of rebound following ISCO using data from 7 sites that had at least 1 year of post-treatment monitoring data. Rebound (defined as an increase of at least 25% in parent CVOC concentration during the post-treatment period) occurred in 13 of the 16 wells (81%) analyzed from the 7 sites; however, the median percent reduction decreased to 78% at the end of the record from 90% observed immediately after remediation. Krembs (2008) reported that rebound (defined as an increase of at least 25% in post-remediation concentrations at least 1 year after treatment) occurred at 71 of 116 sites (62%).

In a survey of chlorinated-solvent site managers (Geosyntec Consultants 2004), respondents reported that rebound was evaluated after remediation at 10 ISCO sites.

4.1.3.2 *In situ chemical reduction*

In situ chemical reduction (ISCR) is considered a chemical/biological technology due to the wide range of mechanisms that can destroy chlorinated-solvent contaminants. Reactions of contaminants with zero-valent iron (ZVI, a reductant commonly used in ISCR) include direct reduction via hydrogenolysis, dehydrochlorination, or beta elimination (e.g., Roberts et al. 1996, Arnold and Roberts 2000), as well as indirect effects of iron corrosion, such as alkaline hydrolysis of certain contaminants such as carbon disulfide resulting from elevated pH in ZVI treatment zones. Reducing agents can be delivered to the subsurface via injection, hydraulic or pneumatic fracturing, and soil mixing.

As with ISCO, a wide variety of approaches and treatment reagents is available. For example, direct treatment of source areas using nanoscale ZVI is a recent development, although there are relatively few case studies or long-term performance evaluations. In an alternative approach, ZVI and clay can be blended into soil (e.g., Sale and Newell 2011), resulting in direct treatment (via reaction with ZVI) as well as reduced mass flux (due to reduced hydraulic conductivity from the clay). ISCR also can be implemented as a containment technology (see Section 4.1.4.3). ISCR reagents may have a very long lifetime in the subsurface and thus remain active and also influence site chemical and hydrologic conditions long after injection.

ISCR was applied at 6 of 118 sites (5%) in a survey of DNAPL source zone treatment results (Geosyntec Consultants 2004). Soil mixing with ZVI and clay had a median percent reduction in soil concentration of 98% (1.7 OoMs) based on data from four sites (Olson and Sale 2009). Data on EPA's CLU-IN website indicate nanoscale ZVI has been used for at least five projects (<http://clu.in.org/download/remed/nano-site-list.pdf>). ISCR (nanoscale ZVI) was a component of one (less than 1%) out of 627 groundwater plume treatment decision documents at Superfund sites from fiscal years 2005–2008 (USEPA n.d.) although not all of these sites contain DNAPL (DNAPL sites were not separately identified in the Superfund remedy data). Respondents to a survey by Geosyntec Consultants (2004) indicated data were available to assess mass removal for only one ZVI site, which was identified as a pilot test of emulsified ZVI and for which the estimated mass reduction was 25%–50%.

4.1.3.3 *In situ bioremediation*

In situ bioremediation (ISB), often referred to as “engineered bioremediation,” involves biological transformation of contaminants, preferably (but not always) to less harmful intermediate and final compounds. Microbes may use contaminants as electron acceptors or as electron donors under a wide variety of conditions. ISB can be applied under aerobic conditions (primarily applicable to aromatic compounds) or anaerobic conditions (primarily applicable to chlorinated aliphatic compounds such as TCE or trichloroethane). ISB may involve injection of substrates to supply bacteria with fermentable sources of carbon and other nutrients to produce hydrogen for dechlorinating bacteria (biostimulation) or injection of nonnative microbes (bioaugmentation).

ISB technologies are applicable across a wide range of concentrations. Historically, ISB has been considered most applicable for dissolved plumes. However, the feasibility of bioremediation in DNAPL source zones has been recognized recently (ITRC 2008b). ISB also can be readily coupled with other technologies. For example, ISB is commonly applied as a plume remediation technology coupled with a more aggressive source remedy, such as ISCO, thermal treatment, and excavation. ISB is also commonly used in residual source areas after more aggressive source remedies are implemented.

ISB was applied at 25 of 118 sites (21%) in a survey of DNAPL source zone treatment results (Geosyntec Consultants 2004). ISB was a component of 53 of 230 (23%) source treatment and 62 of 627 (10%) groundwater plume treatment decision

documents at Superfund sites from fiscal years 2005–2008 ([USEPA n.d.](#)) although not all of these sites contain DNAPL (DNAPL sites were not separately identified in the Superfund remedy data).

McGuire, McDade, and Newell ([2006](#)) compiled performance data from 26 sites containing DNAPL treated with ISB. The resulting data indicated a median reduction of 95% (1.3 OoMs) with a range of 29%–99.9% for parent CVOC concentration; however, reductions were reduced to a median of 62% (0.4 OoMs) and a range from 150% (indicating a 150% increase in post-treatment concentration relative to pre-treatment concentration) to 99.7% in total CVOC concentrations (total CVOCs include CVOCs produced as degradation products from the parent compounds). McGuire, McDade, and Newell ([2006](#)) included both pilot-scale and full-scale applications in their performance analysis. Respondents to a survey by Geosyntec Consultants ([2004](#)) indicated data were available to assess mass removal for 1 ISB site, for which mass removal was identified as greater than 90% and rebound was not observed.

McGuire, McDade, and Newell ([2006](#)) performed a detailed analysis of rebound following ISB using data from 10 sites that had at least 1 year of post-treatment monitoring data. Rebound (defined as an increase of at least 25% in parent CVOC concentration during the post-treatment period) occurred in 4 of the 20 wells (20%) analyzed from the 10 sites; however, the median percent reduction in the parent CVOCs increased to 96% at the end of the record from 77% observed immediately after remediation (total CVOCs was not reported). The site data used by McGuire, McDade, and Newell ([2006](#)) did not determine whether the substrate used for ISB was still active (and thus active remediation still occurring) at the time rebound was assessed. Based on a survey of chlorinated-solvent site managers ([Geosyntec Consultants 2004](#)), respondents reported that rebound was evaluated after remediation at 3 ISB sites. Rebound was not reported at any of those sites.

4.1.3.4 Monitored natural attenuation

As defined by the USEPA ([1998, 1999](#)), natural attenuation includes physical, chemical, or biological processes that act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or groundwater. Examples of these in situ processes include biodegradation, dispersion, dilution, sorption, volatilization, and chemical or biological stabilization, transformation, or destruction of contaminants ([Wiedemeier et al. 1999](#)). MNA implies that remediation progress is periodically assessed to ensure that the remedy is operating as planned, for example, that plumes are not expanding and that there are no new or increasing threats to human health and the environment. Active remediation technologies rarely achieve complete remediation of all contaminant mass; thus, in effect, MNA is typically a component of every chlorinated-solvent site remedy ([ITRC 2008a](#)).

MNA was a component of 116 of 627 (19%) groundwater plume treatment decision documents at Superfund sites from fiscal years 2005–2008 ([USEPA n.d.](#)) although not all of these sites contain DNAPL (DNAPL sites were not separately identified in the Superfund remedy data). McGuire et al. ([2004](#)) compiled data for 191 sites at which MNA was considered and found that MNA was precluded at 23% of the sites due primarily to the presence of an expanding plume or long remediation time frames. McGuire et al. ([2004](#)) further reported that MNA is the sole remedy at 30% of the sites and MNA coupled with source remediation is being implemented at 33% of the sites.

Newell et al. ([2006](#)) analyzed temporal records from 47 monitoring wells at 23 chlorinated-solvent sites to determine whether MNA was occurring. The median reduction in total CVOC concentration was 74% (0.6 OoMs) over 9 years of monitoring, with a maximum reduction of 99.2% in 11 years; however, about 10% of the sites exhibited increasing concentrations ranging 35%–1200%.

4.1.4 Containment

The objective of containment technologies is to prevent or reduce mass discharge from a source. Little or no direct treatment of the source results from application of these technologies. Containment remedies should consider the possibility of back-diffusion from silt and clay zones downgradient of the containment system location, which could result in sustained VOC concentrations downgradient from the contained source area for some time.

4.1.4.1 Pump and treat

Extraction wells are typically installed with their screen intervals intersecting the contaminant plume. Pumps extract groundwater, which is treated above grade using various technologies (e.g., air stripping, carbon absorption, condensation, or oxidative destruction). P&T is generally effective for removal of aqueous-phase contamination and thus is commonly used as a plume capture and containment remedy because extraction wells positioned downgradient from sources intercept a migrating plume and prevent further downgradient contaminant migration ([NRC 1997](#)). P&T is generally ineffective for removal of vapor, sorbed-phase contamination, and DNAPL sources, although there are possible exceptions in aquifers with

little or no matrix storage, such as bedrock.

Although P&T is considered here under containment technologies, pumping wells located near a source zone can accelerate mass dissolution from DNAPL and thus expedite source area depletion. An example of this approach is the Gold Coast site (see [Text Box 4-3](#)). The key to this approach appears to be substantively increasing the hydraulic gradient through the DNAPL source zone. P&T was applied at 1 of 118 sites (less than 1%) in a survey of DNAPL source zone treatment results ([Geosyntec Consultants 2004](#)). P&T was a component of 83 of 627 (13%)

Text Box 4-3. Gold Coast Case Example, Pump and Treat Used as a Containment Technology (see Appendix A)

The Gold Coast site provides an example of using pump and treat for containment. Discharge to the subsurface occurred between 1970 and 1982; pump and treat started with 21 extraction wells in 1990. The porous limestone formation facilitated groundwater extraction, with 25 million gallons treated in the first year at an average pumping rate of 48 gpm. The concentrations of TCE and PCE were reduced to 6 µg/L and 24 µg/L, respectively, and confined to a 200 square foot area. The pump-and treat-system was shut down in 1994 after groundwater VOC concentrations were not reduced further, and air sparging was then conducted, resulting in reduction of concentrations below MCLs. In this case study, a small source mass was present due to limited operations, the limestone formation resulted in little back-diffusion, and the large number of extraction wells probably enhanced flushing and NAPL depletion, which resulted in quicker cleanup.

groundwater plume treatment decision documents at Superfund sites from fiscal years 2005–2008 ([USEPA n.d.](#)), although not all of these sites contain DNAPL (DNAPL sites were not separately identified in the Superfund remedy data).

A USEPA study of multiple P&T systems ([USEPA 1999](#)) provided performance data in the form of reduction in maximum concentration for eight systems. The eight sites represented a wide range of hydrogeologic and source conditions and had been operating for an average of 6 years. The contaminant concentration reduction range for eight sites was between 16% and 99%, with a median percent reduction concentration of 88% (0.9 OoMs).

4.1.4.2 Permeable reactive barriers

PRBs are typically constructed of a material that directly or indirectly destroys dissolved contaminants passing through the barrier due to groundwater advection ([ITRC 2000a](#)). PRBs typically contain a chemically or biologically active treatment medium and thus may also be considered a chemical or biological treatment technology. However, PRBs are considered a containment technology because the primary intent is to enclose a plume or source and destroy or degrade contaminants in the groundwater as the water passes through the barrier. PRBs are commonly constructed with ZVI (described in Section 4.1.3.2). PRBs may also be employed in combination with source containment technologies such as “funnel and gate” configurations as described in Section 4.1.4.3.

Several key issues in site characterization and in the PRB design and construction have been identified that affect performance and longevity of PRBs ([ITRC 2005a](#)). Those issues include reduced permeability of the PRB resulting from construction methods, preferential flow pathways in the reactive media, and inaccurate or incomplete hydrologic characterization. However, typical estimates of PRB lifetimes for ZVI range 10–30 years. An important factor for consideration in assessment of PRB performance is that even if a PRB is 100% efficient in destroying all VOCs in groundwater passing through it, VOC concentrations in groundwater downgradient from the PRB may respond slowly due to long-term desorption of VOCs from low-permeability strata.

PRBs were a component of 8 of 627 (1%) groundwater plume treatment decision documents at Superfund sites from fiscal years 2005–2008 ([USEPA n.d.](#)), although not all of these sites contain DNAPL (DNAPL sites were not separately identified in the Superfund remedy data). Data from a vendor for ZVI PRBs (Envirometal Technologies, Inc.) indicates that more than 200 PRBs have been constructed worldwide ([ITRC, 2011](#)).

Published multisite studies of PRB performance were not identified. A multisite study of ZVI PRBs performed for the REMChlor model ([Liang et al. 2010](#)) compiled performance data for TCE removal from six sites with ZVI PRBs. The median percent removal of TCE was 84% (0.8 OoMs), with the minimum and maximum of 22% and 99.9%, respectively. The same study compiled performance data from six mulch-wall PRBs and showed the median percent removal of TCE concentration was 82% (0.7 OoMs), with the minimum and maximum of 60% and 99.5%, respectively.

4.1.4.3 Low-permeability barrier walls

Low-permeability barrier walls are designed to prevent or control migration of fluids into and/or from the contained area. A common complement to low-permeability barriers is extraction of groundwater from within the contained area to maintain an inward hydraulic gradient. Examples of low-permeability walls are sheet pile barriers and slurry walls. Sheet piling can be driven into the subsurface. Individual sheets are joined together. Slurry walls are a trench in which a slurry of soil-bentonite or soil-cement is placed. The wall or trench may either fully or partially enclose the source. In either case, the wall or trench is commonly keyed into an underlying low-permeability zone to prevent or reduce seepage of groundwater or chlorinated solvent into or from the enclosed area. There is no active treatment by the walls. Low-permeability barrier walls may be used in combination with other source and plume treatment technologies. For example, an impermeable barrier may be used to isolate a concentrated source area, coupled with ISB or another technology to address a dissolved plume outside the contained area. Impermeable barriers may also be used to divert flow through discrete treatment zones. For example, in a configuration known as a “funnel and gate,” low-permeability barriers are oriented to divert groundwater to a permeable section containing ZVI or other reactive material to treat the diverted groundwater.

Source area containment and vertical engineered barriers were a component of 80 of 362 (22%) source treatment remedies (including source remedies with treatment and without treatment) and 15 of 627 (2%) groundwater plume treatment decision documents at Superfund sites from fiscal years 2005–2008 ([USEPA n.d.](#)), although not all of these sites contain DNAPL (DNAPL sites were not separately identified in the Superfund remedy data).

USEPA ([1998](#)) evaluated the performance of vertical low-permeability barrier walls at 24 sites. Seventeen of those sites included groundwater extraction to maintain an inward hydraulic gradient. Twenty-one of the sites were soil-bentonite barriers, and the remaining barriers were cement-bentonite, clay, or vibrating beam walls. The study found that 83% of the sites met design objectives and performed satisfactorily. The most significant factor in poor performance was leakage near areas where the walls were keyed into underlying low-permeability barrier layers.

4.1.4.4 Solidification/stabilization

“Solidification” refers to processes that change the physical properties of contaminated media by increasing compressive strength, decreasing permeability, and/or encapsulating the contaminants to form a solid material. “Stabilization” refers to processes that involve chemical reactions to reduce the mobility of a waste. Solidification/stabilization (S/S) treatment typically involves injecting or mixing (in situ or ex situ) a binding agent or chemical reagent into the contaminated media. Typical treatment objectives are to achieve very low hydraulic conductivity (typically

$<1 \times 10^{-6}$ cm/sec) and leachate concentrations for contaminants of concern in compliance with regulatory criteria.

S/S is one of the most frequently used remedies at Superfund sites. In situ S/S remedies were a component of 15 (7%) and ex situ S/S remedies were a component of 33 (14%) out of 230 source treatment remedy decision documents at Superfund sites from fiscal years 2005–2008 ([USEPA n.d.](#)) although not all of these sites contain DNAPL (DNAPL sites were not separately identified in the Superfund remedy data).

USEPA ([2009a](#)) recently reviewed performance of seven S/S sites, although none of the sites was primarily a chlorinated-solvent DNAPL site. Five-year reviews for sites treated as early as 1993 indicated that the remedies continue to operate as designed. At one of those sites, a manufactured gas plant site that was treated in 1993, cores of the treated soil were collected 10 years after treatment and analyzed for chemical and physical deterioration. Results of the study concluded that the S/S-treated material at the site continues to exceed the original performance standards.

4.2 Rationale for Coupling Technologies

Early remedial designs commonly employed a single technology to address a contaminant source or plume or both, with the expectation that one technology was applicable over the full remediation life cycle from initial construction through regulatory closure. Unfortunately, changes in site conditions due to remediation, natural attenuation, and contaminant transport mechanisms were not well understood. As a result, the single-technology approach was found to be unsatisfactory in most cases. In hindsight, this outcome was not unexpected for several reasons:

- Contaminant mass, mass fluxes, and concentrations, as well as other site conditions such as geochemistry and hydrology, changed over time as a result of remediation, natural attenuation, or other site activities and processes. As a result, operational parameters often needed to change to a greater degree than remedial operations could be

- Remedial objectives changed as regulations and our understanding of risk control or management
- Multiple contaminants or classes of contaminants (e.g., CVOCs, petroleum VOCs, semivolatile organic compound [SVOCs], metals, polychlorinated biphenyls, and pesticides) were often comingled in a source zone or immediately downgradient; thus, a single technology could not address all contaminants present in many

Text Box 4-4. Launch Complex 34, Sequential Treatment Compared to Individual Technologies (see Appendix A)

A cost analysis at full scale was prepared by comparing the life-cycle costs of sequential ISCO/ISB compared to P&T, ISCO only, and ISB only, based on a theoretical site with a 100-foot-long, 100-foot-wide source area with 12,500 pounds of TCE (sum of TCE as DNAPL, on soil and at approximately 175 mg/L in groundwater) present 10–80 feet bgs. The geology was assumed to be composed of a sand unit 10–40 feet bgs and a silty sand unit 40–80 feet bgs. The cost analysis suggests that all in situ alternatives have lower lifetime costs than P&T, providing that they have short operating durations. While the sequential ISCO/ISB option has a higher life-cycle cost than ISB alone, the shorter lifetime of a sequential approach may make it more advantageous than ISB alone. Over 75% of the ISB costs in the sequential approach were driven by the donor demand associated with the aggressive permanganate dose.

More recently, the remedial paradigm has shifted to accept that more than one technology is almost always necessary over the treatment life cycle or at different locations within a source area or plume. Remedial designers and chlorinated-solvent site managers recognize that coupling technologies into sequences, combinations, or treatment trains, can more effectively reduce contaminant concentrations and project duration than individual methods, particularly at complex source zones containing DNAPL or multiple contaminants (see [Text Box 4-4](#)). An approach for coupling technologies needs to be developed prior to implementing the remedial action rather than as a response to an underperforming remedy; however, the overall approach should be adaptive and allow for modifications to optimize remedies and transition between remedies based on evolving site conditions.

4.2.1 Spatial Temporal Coupling of Technologies

Combining technologies spatially and/or temporally requires active management of the overall remediation strategy, making process control decisions for individual remedies while treatment is under way and deciding when and how to transition from one remedy to the next. Three approaches of how multiple technologies may be coupled to address a contaminated site include the following:

- Temporal (i.e., sequential) coupling of technologies, where the first technology is replaced by a more cost-effective technology after the point of diminishing returns for the initial technology or where different contaminants are addressed at different times using different technologies. Examples of this approach include thermal treatment of a source zone followed by MNA and ISCO of a source area followed by bioremediation. The U.S. Navy has recognized and described ([NAVFAC 2004](#)) the use of treatment trains (i.e., technologies coupled sequentially over time) for remediation of complex sites:

A treatment train that combines both an active and a passive remedial approach is an important strategy for achieving cost-effective site cleanup. The use of passive remedial technologies is likely an important component of site cleanup because of the difficulty in cost-effectively treating contaminants that are trapped in the subsurface. These contaminants are often trapped within low-permeability layers or in pore spaces and their release rate is slow and diffusion controlled. Examples of this approach are the application of air sparging or chemical oxidation to reduce elevated source area concentrations followed by MNA for groundwater contaminated with dissolved organic compounds. The concurrent implementation of multiple technologies may also be effective such as LNAPL removal coupled with the downgradient application of MNA.

- Simultaneous technology implementation, where multiple processes or technologies are applied to address different contaminants at the same time. An example of this approach is a treatment train used for a P&T system where an air stripper is used to remove high concentrations of chlorinated solvents from the extracted groundwater and those that remain are adsorbed onto activated carbon during a polishing
- Spatial technology implementation (i.e., spatial coupling of technologies) where different technologies are applied to different regions of the site, such as the source and the plume. Examples of this approach include (a) thermal treatment of a source zone and anaerobic biodegradation of the downgradient groundwater plume, (b) containment of a source zone and MNA of the downgradient groundwater plume, and (c) vadose zone and

saturated zone treatment.

Based on the authors' experience, the coupling of technologies is most commonly accomplished by the following:

- Intensive technology followed by more passive methods—For example, at some sites vadose zone treatment using active SVE (with blowers and vapor treatment system) has been replaced by passive SVE methods such as microblowers, barometric pumping, or other low-energy or passive means ([Kamath et al. 2009](#)).
- Source technology and plume technology—Source zone management using one approach (such as containment with a PRB or an intensive in situ technology) and plume management using another approach (such as P&T or ISB).
- Any technology followed by MNA. In general, performance data from multiple site studies show that a single application of current-generation remediation technologies is not likely to achieve low part-per-billion drinking water standards. Therefore, active remediation at many or perhaps most sites will be followed by MNA of residual

All remedial technologies affect site conditions and, therefore, may impact other technologies applied at the site. Thus, the impact of technologies on each other must be considered. However, in many instances the potential direct or indirect effects of one technology on another have been overestimated. For example, in the past application of a technology that significantly changed groundwater conditions (e.g., pH, redox potential [Eh], or dissolved oxygen) was expected to permanently eliminate coupling with another technology that requires opposing conditions. This has proven to not be the case. Field and laboratory research indicate that, in general, the impacts of technologies that strongly affect groundwater conditions during treatment are often transient; once the active treatment is complete, groundwater chemical conditions generally trend towards a steady-state condition. As a result, combinations of technologies that might be considered opposing (e.g., ISCO and anaerobic bioremediation) have been found to be very effective if groundwater conditions are carefully managed. Thoughtful treatment train and remedial system design and operation should enable project management to create desired conditions and achieve project goals more quickly and economically than continued application of the original technology.

4.2.2 Technology Compatibility

The selection, design, and application of two or more remedial technologies sequentially (in series) or concurrently (in parallel) in time or space should consider the following:

- conditions required for optimum performance of each individual technology
- by-products of individual technologies
- impacts of technology by-products on the second technology or its by-products

For example, when considering reaction-based remedies, more energetic methods typically are applied first because the large contaminant mass initially present increases the probability that a reagent molecule will encounter and destroy a contaminant molecule. Conversely, more persistent methods may best be applied later when rebound and back-diffusion are of concern. [Table 4-2](#) describes additional examples. Many have been observed in the field or laboratory; others are suspected but not documented to date.

On a conceptual level, the following sequential combinations of remediation technologies are identified as being “compatible” or “incompatible” with respect to the first technology being applied, followed by the second technology. Note this compatibility matrix is very general, is primarily geared to source zones, and may not apply to all sites. Nonetheless, [Table 4-2](#) presents current thinking and recent experience regarding maximization of remediation. Two technologies may be compatible (i.e., the use of one does not adversely impact the performance of the other) or synergistic (i.e., the use of one improves the performance of the other). Synergy increases the overall rate of remediation; compatibility does not affect the overall rate of remediation. The order in which two technologies are implemented affects their compatibility or synergy to a degree. Therefore, the notes below the table are written from the perspective that the technology discussed is applied first or upgradient, and potential coupling technologies are applied second or downgradient.

4.3 Transitioning Between Technologies

As outlined in [Section 4.2](#), remedial designers and chlorinated-solvent site managers today generally realize that most sites require coupling multiple technologies in time or space to make satisfactory progress towards or to achieve functional and absolute objectives. Treatment trains require an assessment of the compatibility of individual technologies, which was

described in Section 4.2.2. The next step is to develop a strategy on how and when to transition between technologies.

Table 4-2. Technology compatibility matrix

<div>Followed by this technology or in downgradient area</div> <div>↓</div> <div>Apply this technology first or in upgradient area</div> <div>→</div>		Physical removal technologies			Chemical/biological technologies			Containment technologies		
		Surfactant/ cosolvent flushing	Thermal technologies	Other extractive technologies	Chemical oxidation	Chemical reduction	Bioremediation	Monitored natural attenuation	Permeable reactive walls	Other containment technologies
Physical removal technologies	Surfactant/ cosolvent flushing		Potentially compatible but not an anticipated couple (see Note 1)			Generally compatible (see Note 1)		Potentially compatible but not an anticipated couple (see Note 1)		
	Thermal technologies	Potentially compatible but not an anticipated couple (see Note 2)		Potentially compatible but not an anticipated couple (see Note 2)			Generally compatible (see Note 1)		Potentially compatible but not an anticipated couple (see Note 2)	
	Other extractive technologies	Potentially compatible but not an anticipated couple (see Note 3)			Generally compatible (see Note 3)				Potentially compatible but not an anticipated couple (see Note 3)	
Chemical/biological technologies	In situ chemical oxidation	Potentially compatible but not an anticipated couple (see Note 4)				Potentially compatible but not an anticipated couple (see Note 4)	Generally compatible but requires consideration of chemical reagents (see Note 4)		Potentially compatible but not an anticipated couple (see Note 4)	Generally compatible (see Note 4)
	In situ chemical reduction	Potentially compatible but not an anticipated couple (see Note 5)			Likely incompatible (see Note 5)		Potentially Compatible (see Note 5)			
	Engineered bioremediation	Potentially compatible but not an anticipated couple (see Note 6)			Compatibility varies (see Note 6)	Potentially compatible but not an anticipated couple (see Note 6)		Generally compatible (see Note 6)	Potentially compatible but not an anticipated couple (see Note 6)	
	Monitored natural attenuation	Potentially compatible but not an anticipated couple (see Note 7)							Potentially compatible but not an anticipated couple (see Note 7)	
Containment technologies	Permeable reactive barriers	Potentially compatible but not an anticipated couple (see Note 8)			Likely incompatible (see Note 8)	Potentially compatible but not an anticipated couple (see Note 8)				Potentially compatible but not an anticipated couple (see Note 8)
	Other containment technologies	Potentially compatible but not an anticipated couple (see Note 9)								

Table 4-2 Notes

- Enhanced extraction by surfactant/cosolvent flushing is generally compatible with anaerobic bioremediation and with MNA because residual surfactant or cosolvent can act as an electron donor. Surfactant/cosolvent flushing is anticipated to be compatible with other physical removal technologies and with containment technologies; however, these are not anticipated couples because surfactant/cosolvent flushing is typically designed to eliminate nonaqueous- phase liquid (NAPL) with an anticipation that further treatment (other than potentially bioremediation or MNA) is not
- Thermal technologies are generally compatible with engineered bioremediation and with MNA. The microbial population may be reduced during the active thermal treatment phase although residual warmer temperatures after treatment and in fringe areas may result in rapid recovery and/or enhanced growth (e.g., [Iqbal, Metosh-Dickey, and Portier 2007](#)). A potentially promising couple may be to use the heat associated with a thermal technology to activate sodium persulfate ISCO. Thermal technologies are anticipated to be compatible with other physical removal technologies and with containment technologies such as ZVI reactive barriers (e.g., [Truex et al. 2011](#)); however, these are not anticipated couples because thermal technologies are typically designed to dramatically reduce source areas contaminant concentrations with the anticipation that further source area treatment (other than potentially bioremediation or MNA) is not
- Other extractive technologies (e.g., excavation, MPE, etc.) for source removal are generally compatible with thermal, chemical/biological, and containment technologies. However, these technologies probably would not be intentionally coupled sequentially unless the second technology (i.e., ISCO, ISCR, bioremediation, or MNA) is intended to address residual or inaccessible NAPL-, sorbed-, and or dissolved-phase contaminants that were not removed by the extractive
- ISCO is commonly coupled with engineered bioremediation (aerobic and anaerobic) and MNA (e.g., Bryant and Haghebaert 2008), which address contaminants that were not destroyed by the ISCO; however, the impact of chemical reagent by-products (e.g., sulfate from persulfate-based ISCO, pH shifts, etc.) must be considered in

the design of the engineered bioremediation and in the planning of the monitoring of both bioremediation and MNA. Chemical oxidants may also be coupled with surfactants. ISCO is potentially compatible with physical removal technologies; however, ISCO probably would not be coupled sequentially with excavation because both typically address source areas. ISCO may reduce the fouling of P&T extraction wells (another extractive technique) by promoting the precipitation of iron, manganese, and other inorganics and by increasing the redox potential before the groundwater enters the well. ISCO is potentially compatible with ISCR and PRBs. However, in the case of ISCR, the oxidant must be consumed prior to introduction of the reductant to prevent wasteful chemical reactions. Similarly, ISCO increases reductant reagent requirements, even if only to re-reduce naturally reduced inorganic compounds in the subsurface that were oxidized and mobilized during ISCO. ISCO is anticipated to be compatible with other containment methods, but the remedial design and operation must ensure that all oxidant is consumed and, ideally, that groundwater has returned to background conditions before it reaches a PRB intended to encourage reductive processes. Thermal technologies may be used to catalyze persulfate. Finally, ISCO has been coupled with in situ stabilization to address residual source areas that are inaccessible for

5. ISCR is an emerging technology with few well-documented applications. A combination of ZVI and clay is one example of this technology ([Puls, Olsen, and Sale 2006](#)). The injection of reductant solutions (e.g., sodium dithionite, metabisulfide, calcium polysulfide, etc.) to reduce metals in groundwater, which are not the focus of this document but also may be treated at a complex site, is another. The IDSS Team considers that ISCR is compatible with physical removal technologies, e.g., excavation and disposal. However, it should be recognized that reductant reagents may mobilize naturally oxidized components of the subsurface (e.g., iron and manganese oxides, hydroxides, etc.) that may foul P&T extraction wells if groundwater conditions do not return to background conditions before the groundwater enters and is reoxygenated in the well. Regardless, these technologies probably would not be intentionally coupled sequentially because ISCR typically treats source areas that would not be effectively addressed with removal technologies after the ISCR was complete. Similarly, ISCR is potentially synergistic and compatible, respectively, with PRBs intended to encourage reductive processes and with other containment technologies that are not adversely impacted by reducing groundwater. ISCR is potentially synergistic with anaerobic bioremediation or MNA if parent chlorinated solvents, which are biodegraded best under reducing conditions, are present. ISCR is theoretically compatible with ISCO, but chemical reactions may consume both ISCR and ISCO reagents without destroying the targeted contaminants.
6. Engineered bioremediation is compatible and/or synergistic and commonly applied sequentially in time or space with MNA. Engineered bioremediation is potentially compatible with physical removal technologies, containment technologies, and chemical reduction; however, these are not anticipated couples. The compatibility of engineered bioremediation with ISCO varies on a site basis because conditions created during bioremediation consumes ISCO reagents until neutralized. For example, an organic substrate introduced to enhance anaerobic bioremediation creates reducing conditions and reduces previously oxidized inorganic compounds. Both increase the oxidant demand of the subsurface, which has to be satisfied before ISCO can proceed. The mass of ISCO reagent required may become cost-prohibitive. In contrast, use of a chemical reagent for aerobic bioremediation may be readily coupled with persulfate-based ISCO because the high pH conditions resulting from the aerobic bioremediation agent may catalyze high pH-activation of the persulfate for MNA is potentially compatible with all other technologies, and in most chlorinated solvent remediation sites
7. MNA is a sequential component of the remedy following source reduction or downgradient of a more aggressive technology. However, following MNA with any other technology is not an anticipated couple because MNA would not be effective over reasonable time scales at a chlorinated-solvent.
8. PRBs are typically compatible with other technologies though the performance of PRBs that promote destruction of chlorinated solvents by reductive processes would be compromised by groundwater containing residual ISCO reagents or exhibiting highly oxidizing conditions after ISCO. It is unlikely that the other technologies in [Table 4-2](#) will be applied after a PRB at the same location because the barrier addresses dissolved-phase contaminants in a migrating plume, while most of the other remedial methods more effectively address higher contaminant concentrations. The exception is the combination of a PRB and a slurry or sheet pile wall to form a funnel-and-gate groundwater treatment
9. Containment technologies are generally compatible with all other technologies. Nonetheless, it is unlikely that a containment technology will be succeeded by another technology unless the containment technology has been found to be ineffective or remediation objectives have.

Text Box 4-5. Pemaco, Treatment Transitions (see Appendix A)

To meet RAOs within 5 years, thermal treatment was used on the highly contaminated soil and groundwater in the source zone. The 2005 record of decision (ROD) divides the Pemaco site into the following: The “surface and near-surface soil remediation zone”—Remedy for this zone is soil cover and revegetation. · The “upper vadose zone soil and perched groundwater”—Remedy for this zone is high-vacuum dual-phase extraction. · The “lower vadose zone soil and Exposition zone groundwater”—This is considered the source area of the site; the most highly contaminated soil is found here, as well as the dissolved-phase groundwater plume. The remedy for the lower zone is ERH with vapor extraction, vacuum-enhanced groundwater extraction, and groundwater pump and treat, followed by MNA. The ROD stated that ERH would be applied within the 10,000 µg/L TCE groundwater contour, with electrodes installed as deep as 100 feet bgs.

In the typical approach of the past, in which a single technology was expected to achieve all project goals, a remedy was operated until it was simply no longer effective. For example, a P&T system would be operated until an asymptotic VOC concentration was reached, at which point an argument might be made that nothing more can be done or that the remedy has failed. Under the new paradigm of coupling technologies with an adaptive strategy, the treatment train can be conceptually developed prior to implementing the remedial action and then adapted based upon evolving site conditions (see [Text Box 4-5](#)). This approach requires development of an appropriate monitoring plan to determine when to make the planned transition between technologies. Under a more common scenario in which a remedy (or remedies) has already been implemented, then the monitoring approach should be frequently assessed and optimized to ensure that it is appropriate to determine when a remedy has reached its limit of effectiveness or is underperforming. Also, it is possible to identify and quantify transition triggers after a sequence of remedial methods has been developed. Possible transition triggers are as follows:

- contaminant concentrations in one or more phases most likely to be contacted by the public or environment
- contaminant concentrations in a single phase, particularly the percentage of aqueous-phase solubility
- contaminant phase, particularly the presence of free phase
- contaminant lineage—parent compounds, which are normally more readily degraded under reducing conditions, versus daughter compounds, which are more readily degraded under oxidizing conditions
- site conditions created during method execution (for example, lower pH or Eh or higher dissolved-phase concentrations of contaminants and inorganics [e.g., metals, dissolved solids] following Fenton’s reagent or electron donor injection)
- cost per unit of contaminant destroyed

As described in Section 4.2.1, one of the most common treatment trains used in chlorinated- solvent site remediation and management is to follow any aggressive source remedy with MNA. A protocol to bridge the transition from an aggressive remedy to MNA was developed by the ITRC ([ITRC 2008a](#)) and can be adapted to guide the transition between any technologies. The strategy is illustrated using the eight steps in Figure 4-1.

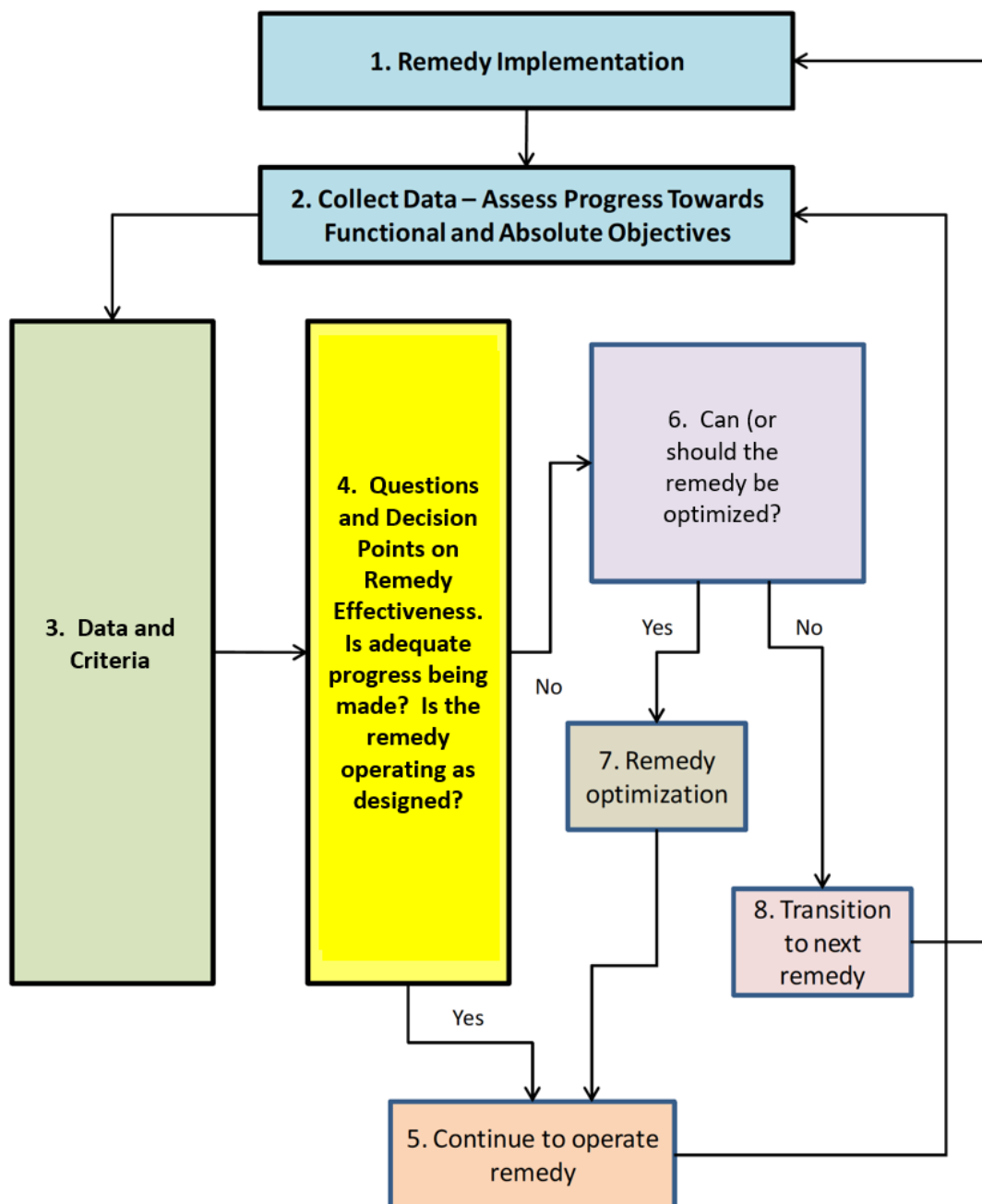


Figure 4-1. Remedy transition flowchart.

- Step 1 is remedy implementation. At this point, it is assumed that the site has been characterized, a CSM prepared, and an IDSS strategy
- Step 2 is to collect data. Site data are used to assess progress of the remedy towards the functional and absolute
- Step 3 is to collect characterization data and decision-making information describing risk, evaluating technology performance, treatment time, and cost
- Step 4 provides questions and decision points on remedy effectiveness, such as, “Is adequate progress being made towards the functional objectives?” and, “Is the remedy operating as designed?”
- Step 5 (for an affirmative answer to Step 4) is to continue operating the
- Step 6 (for a negative answer to Step 4) is to evaluate whether the remedy can or should be optimized to improve
- Step 7 (for an affirmative answer to Step 6) is to optimize the remedy and continue operation, with feedback to Step 2 for periodic assessment
- Step 8 (for an affirmative answer to Step 6) is to transition to the next remedy, with a feedback to Step 1 for implementation of the next remedy

4.4 Washington Square Mall Example

The 14-Compartment Model, introduced and described in [Section 2.5](#), was originally developed as a visual depiction of the distribution of up to four phases of a contaminant among saturated and unsaturated and high- and low-permeability media and potential movement between phases and media. The model can also be used to predict, estimate, or evaluate the effect(s) of a remedial technology or technologies on contaminant concentrations in individual compartments and on contaminant fluxes between compartments. These predictions and evaluations are used to identify the following:

- mass transfer between compartments that must be addressed
- mass transfer between compartments that may not be addressed
- complementary methods to address the contaminants that remain after treatment

An online web version of the 14-Compartment Model is now available (Marquardt et al., 2014; search for “14-Compartment Model” “Online” “ESTCP”).

Using the technology mapping approach by Sale and Newell ([2011, Section 4, pp. 65–100](#)), technologies were selected and mapped for the Washington Square Mall example characterized in [Section 2.6](#), and SMART functional objectives were defined in [Section 3.5.3](#). Unsaturated soil at the site is described as clay and silt, with PCE concentrations up to 4000 µg/kg. The former dry cleaner has been demolished, and the site is fully accessible. Depth to water is approximately 5–7 feet bgs, and the clay and silt lithology transitions to silt/sand at a depth of approximately 13 feet. The groundwater aquifer is relatively permeable silt and sand, bounded above and below by lower-permeability silt and clay. The most stringent soil cleanup goal is 40 µg/kg, based on a risk assessment of soil vapor intrusion. The objective established by the property owner is to achieve the most stringent cleanup goal within 6 months.

4.4.1 Treatment Approach for the Unsaturated Zone

Based on the soil lithology, compounds present, and time frame, the technologies that were considered were thermally enhanced SVE, ISCR by soil mixing with ZVI clay, and soil removal; based on cost and time frame, soil removal was selected. Dewatering will lower the water table, which will allow soil excavation to 13 feet and removal of all impacted silt/clay soil. A performance map for the selected technology was prepared using the 14-Compartment Model (Figure 4-2). (See [Section 2.6.2](#) for an example of order-of-magnitude estimates and [Section 4.1.1](#) for performance predictions.)

Numeric values ranging 0–3 were assigned to reflect contaminant concentrations in each compartment. The DNAPL compartments were assigned a value of 0 based on the soil and groundwater concentrations, which indicate a sorbed phase but that a DNAPL phase is unlikely. As expected, the source removal by excavation will achieve all cleanup goals within the soil source zone. A more modest impact, assigned a technology performance of 1, is expected on the dissolved- and sorbed-phase concentrations in the transmissive portion of the plume zone due to elimination of mass flux from the unsaturated zone soil. However, contamination exceeding the cleanup goals will most likely remain within the plume zone. Thus, an additional technology is required to achieve the cleanup goals within the plume zone.

4.4.2 Treatment Approach for the Saturated Zone

In light of the size of the treatment area, aquifer lithology, dissolved contaminant concentrations, and required cleanup duration, ISCO using permanganate (a persistent oxidant) was selected as the plume area remedy. A performance map for the selected technology was prepared using the 14-Compartment Model (Figure 4-3).

Permanganate can readily reduce dissolved and sorbed-phase PCE concentrations in the transmissive portion of the plume and will therefore reduce associated vapor-phase risks. Permanganate will diffuse into the finer-grained silt and clay of the low-permeability zones; thus, a numerical performance of 1 is assigned to the low-permeability aqueous phase and an associated performance of 1 to the low-permeability vapor phase (due to elimination of the groundwater vapor source). Permanganate diffusion is unlikely to be sufficiently thorough to fully address the sorbed-phase impacts in the low-permeability portions of the plume zone. However, sorbed-phase concentrations in the low-permeability portion of the plume zone are expected to be below the required cleanup objective; thus, a residual value in the “After” box does not affect the overall remediation outcome of achieving the cleanup goals.

Zone/ phase	Source						Plume					
	Low permeability			Transmissive			Transmissive			Low permeability		
	Before	Technology performance	After	Before	Technology performance	After	Before	Technology performance	After	Before	Technology performance	After
Vapor	2	3	0	3	3	0	1	0	1	1	0	1
DNAPL	0	3	0	0	3	0						
Aqueous	1	3	0	2	3	0	2	1	1	1	0	1
Sorbed	3	3	0	3	3	0	2	1	1	1	0	1
	0 depicts >1 µg/L in aqueous-phase equivalent			1 depicts >10 µg/L in aqueous-phase equivalent			2 depicts >100 µg/L in aqueous-phase equivalent			3 depicts >1000 µg/L in aqueous-phase equivalent		

Figure 4-2. 14-Compartment Model technology performance map for soil removal at the Washington Square Mall, PCE contamination in soil and groundwater.

Zone/ phase	Source						Plume					
	Low permeability			Transmissive			Transmissive			Low permeability		
	Before	Technology performance	After	Before	Technology performance	After	Before	Technology performance	After	Before	Technology performance	After
Vapor	Not applicable						1	2	0	1	1	0
DNAPL												
Aqueous							2	3	0	1	1	0
Sorbed							2	2	0	1	0	1
	0 depicts >1 µg/L in aqueous-phase equivalent			1 depicts >10 µg/L in aqueous-phase equivalent			2 depicts >100 µg/L in aqueous-phase equivalent			3 depicts >1000 µg/L in aqueous-phase equivalent		

Figure 4-3. 14-Compartment Model technology performance map for permanganate ISCO at the Washington Square Mall, PCE contamination in soil and groundwater.