

CHAPTER 2

THE SOURCE ZONE REMEDIATION CHALLENGE

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2.1 INTRODUCTION

It is well recognized by stakeholders that restoration of soil and groundwater contaminated by organic chemicals in the form of dense nonaqueous phase liquids (DNAPLs) poses major technical, economic and institutional challenges. As of 2012, few case studies of restoration (defined as achieving concentrations at or below maximum contaminant levels [MCLs], thus allowing for unrestricted use and unlimited exposure at the site) have been reported for source zones where DNAPL releases resulted in significant contaminant plumes. While the consequences of DNAPL releases on groundwater quality are easily observed and have been widely documented, the characterization and remediation of DNAPLs in groundwater remain problematic. At many sites, characterization of the location, distribution and amount of DNAPL causing continued groundwater contamination is difficult and often inaccurate (Mercer et al., 2010). Removal or *in situ* destruction of DNAPLs, even when reasonably well characterized, has proven difficult in saturated zones with any significant degree of heterogeneity (Pankow and Cherry, 1996; Kavanaugh et al., 2003; NRC, 2005).

DNAPL sites continue to represent a significant fraction of the sites impacted by chlorinated solvents and other chemicals characterized as DNAPLs. The U.S. Environmental Protection Agency (USEPA, 1993a) evaluated the likelihood of DNAPL presence at 712 National Priorities List (NPL) sites (roughly 55% of all NPL sites as of 1991). At 44 of these 712 sites, DNAPL was observed directly in the subsurface. The likelihood of DNAPL occurrence at the remainder of the sites was estimated based on a detailed analysis of a subset of 310 sites. Extrapolation of the survey results to the universe of NPL sites indicates that approximately 60% of NPL sites (approximately 775 sites) exhibited a high-to-medium likelihood of having DNAPL present as a source of subsurface contamination. Applying the 60% estimate of DNAPL sites to the current (2012) total of approximately 1,700 NPL sites yields 768 DNAPL sites in the current Superfund program. A similar study of 77 dry cleaner sites in Modesto, California, revealed 9 sites (11.7% of sites considered) with a likelihood of DNAPL occurrence based on elevated groundwater and/or soil gas concentrations (S. Carlton, GeoTrans, Inc., Rancho Cordova, California, personal communication, 2013). Considering recent estimates of approximately 36,000 active dry cleaning facilities in the United States, the potential exists for more than 2,800 active or inactive dry cleaner sites in the United States to have DNAPL present in the subsurface.

Since the early 1980s, the USEPA, Department of Energy, Department of Defense, and private industry have recognized that DNAPL site remediation entails significant technical challenges. For example, through early fundamental and applied research directed by the Robert S. Kerr Environmental Research Center, in Ada, Oklahoma, the USEPA prepared

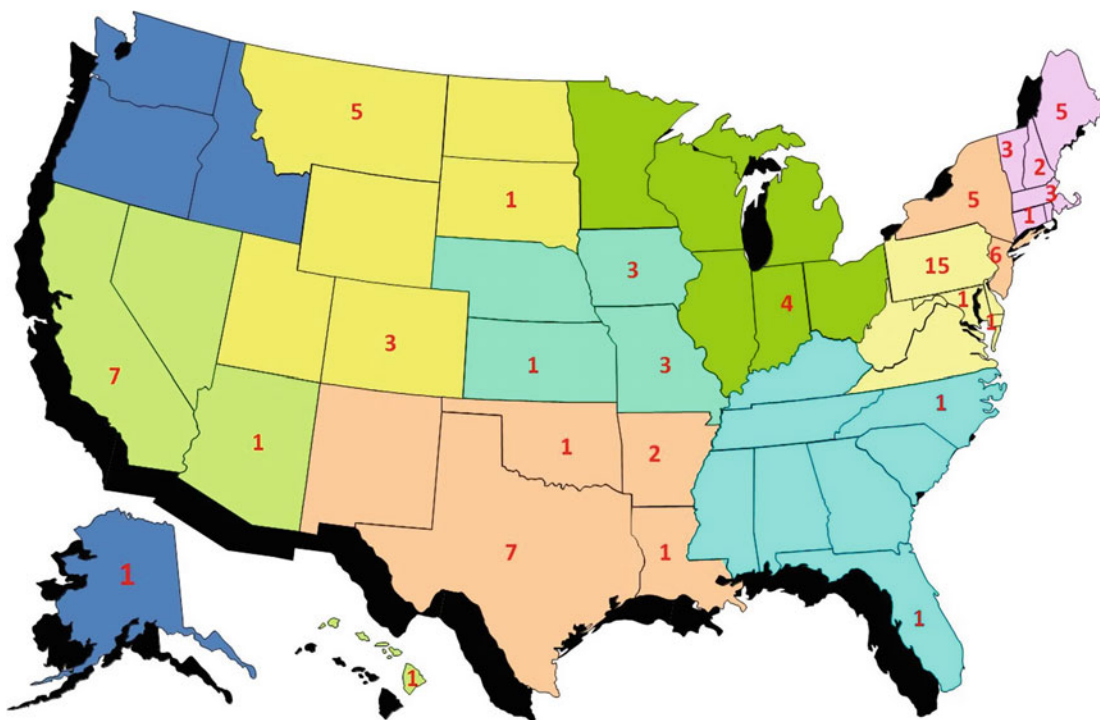


Figure 2.1. Locations of groundwater technical impracticability (TI) waivers. Total is approximately 85 sites as of November 2011. From Charsky, 2012.

numerous technical guidance documents to advise stakeholders on characterization and remediation of DNAPL sites (USEPA, 1994). In addition to relevant guidance documents, USEPA also developed policy guidance in recognition of the technical challenges confronting cleanup of DNAPL sites. The applicable or the relevant and appropriate requirement (ARAR) technical impracticability (TI) waiver guidance document published in 1993 provided USEPA's recommended approach for assessing the feasibility of meeting established performance goals at Superfund and Resource Conservation and Recovery Act (RCRA) sites where remediation was considered impracticable from "an engineering perspective, taking cost into consideration" (USEPA, 1993b). In 2011, USEPA released a clarifying memorandum stating that regulators "should not consider the mere presence of DNAPL alone but should provide a sufficient, science-based justification for invoking a TI waiver" (USEPA, 2011c). This clarification is consistent with the infrequent use of this policy instrument since 1993, with only 85 TI waivers (Figure 2.1) addressing groundwater-contaminated sites granted from a universe of approximately 1,500 Superfund sites as of November 2011 (Environmental Security Technology Certification Program, ESTCP, 2011; Charsky, 2012).

In 1994, a committee established by the National Research Council published *Alternatives for Groundwater Cleanup* (NRC, 1994), summarizing the results of research and practical experiences through 1992 on the use of pump-and-treat technology, the dominant approach at that time for remediation of groundwater contaminated by DNAPLs. Groundwater sites impacted by DNAPLs were considered to be the most difficult sites to remediate (Category 4 in a scale of 1–4). At that time, none of the known or suspected DNAPL sites had achieved required cleanup levels, usually MCLs. While significant technical advances in DNAPL site characterization and remediation technologies have been achieved since 1994 (Stroo et al., 2012), it is difficult to predict the impact of any of the suite of *in situ* technologies now available

to remediate DNAPL source zones on the time frames needed to achieve groundwater remediation performance objectives.

More recent reviews of DNAPL source removal case studies also have shown that significant mass removal can be achieved when DNAPL sources are well defined, but complete restoration to concentration levels that allow for unrestricted use and unlimited exposure in these source areas is difficult (Kavanaugh et al., 2003; NRC, 2005; ITRC, 2011). A recent summary of case studies of DNAPL sites that had met regulatory closure criteria indicated that MCLs were achieved at 4 of the 13 sites (USEPA, 2009). However, even in this study, remedial action objectives (RAOs) other than MCLs were the basis for most decisions on final disposition of the site (no further action or long-term monitoring (LTM)) (Table 2.1). Of the four sites where MCLs were achieved, two were impacted by chlorinated solvents and two were impacted by petroleum hydrocarbons and/or polycyclic aromatic hydrocarbons.

Due in part to the number of sites potentially impacted by DNAPL and the limited number of documented DNAPL sites where the final remedial objectives have been achieved, there is still a lack of consensus regarding the ability of proven or innovative technologies to achieve groundwater remediation performance objectives in source zones at DNAPL sites within a reasonable time frame, and at a cost commensurate with perceived benefits or risk reduction (NRC, 2005). In particular there continues to be a lack of consensus regarding the appropriateness of applying intensive and often costly remediation technologies for DNAPL extraction or destruction in the source zone, if such partial mass removal will not have a quantifiable and substantial impact on the time required to meet RAOs and on the life cycle costs of a containment remedy, such as pump-and-treat.

This chapter summarizes the challenges facing practitioners responsible for selecting, designing and operating source remediation technologies. The chapter starts by briefly describing the general management options and the difficulties associated with predicting the performance of source remediation efforts. The chapter then summarizes the state of the art for source characterization and source remediation technologies and then discusses both the benefits and the risks of source depletion. The chapter concludes with a discussion of the potential impacts of source depletion on the life cycle costs for site management.

2.2 SOURCE MANAGEMENT OPTIONS

While the option of long-term containment at DNAPL-impacted sites has disadvantages, this option may represent the optimal use of financial resources, when considering the time value of money. For many DNAPL sites, given the uncertainties associated with the application of demonstrated or innovative technologies and the risk of insufficient performance, combined with the difficulties of predicting the benefits of partial DNAPL source depletion, potentially responsible parties in both the private sector (industry) and the public sector (government) often have been reluctant to undertake intensive source zone remediation. The current practical consequence of this lack of consensus is that for many DNAPL groundwater-contaminated sites, site remediation strategies are dominated by containment technologies, coupled with LTM. For example, pump-and-treat and monitored natural attenuation (MNA), both of which can contain contaminated sites, were used as groundwater remedies, either alone or in combination, at 71% of 164 Superfund sites between 2005 and 2008. During this same time period, institutional controls were included more often than any other groundwater remedy in site decision documents (USEPA, 2010).

This strategy has been effective at limiting the spread of contaminants at these sites and significantly reducing or even eliminating the risk of human and ecological exposures to these chemicals outside of the source zones. However, failure to remove the DNAPL source from the

Table 2.1. Summary of 2009 USEPA DNAPL Case Studies Reportedly Achieving Maximum Contaminant Levels (MCLs)

Site Name, Location	NAPL Type	Regulatory Oversight Program	Site COCs and RAOs for Groundwater	Technologies Applied	Reported Results	MCLs Achieved?	ICs in Place?
Camelot Cleaners, West Fargo, North Dakota	Chlorinated solvents	USEPA, Region 8 Superfund	COCs: PCE (up to 89,000 µg/L) RAOs: Reduce total VOCs to less than 1,000 µg/L in groundwater	Electrical resistive heating	5,188 pounds of VOC mass removed; groundwater concentrations reduced by 99.98%; all groundwater samples under 1,000 µg/L	No	No
Visalia Pole Yard, Visalia, California	Creosote, diesel with PCP	USEPA Superfund NPL with state lead	COCs and RAOs PCP, RAO: 1 µg/L Benzo(a)pyrene, RAO: 0.2 µg/L TCDD equivalent, RAO: 30 pg/L	Grout wall, P&T, <i>in situ</i> thermal desorption, excavation	1,330,000 pounds of organics recovered; risk-based concentration goals and MCLs met for groundwater	Yes	Yes – Land use restricted
Former Southern California Edison MGP Site, Long Beach, California	Polyaromatic hydrocarbon, petroleum hydrocarbons	Voluntary Action under DTSC Expedited Remedial Action Program	COCs: TPH (912 µg/L) Benzene (4.82 µg/L) Naphthalene (20 µg/L) Benzo(a)pyrene (0.34 µg/L) RAOs: No RAOs specified for groundwater	ISCO (ozonation), excavation	Concentrations of benzo (a)pyrene reduced to below MCL (0.2 µg/L)	Yes	Yes – Land use restricted
Former Cowboy Cleaners Site, Broomfield, Colorado	Chlorinated solvents	Colorado Voluntary Cleanup Program	COCs: PCE (1,900 µg/L) RAOs: No numerical RAO specified	ISCO (potassium permanganate)	PCE concentrations in source area reduced to 48 µg/L	No	Yes – Land use restricted
Dry Clean USA No. 11502, Orlando, Florida	Chlorinated solvents	Florida Department of Environmental Protection Dry Cleaning Program	COCs: PCE (27,300 µg/L) RAOs: Reduce PCE in groundwater to 3 µg/L (Florida MCL)	ISCO (hydrogen peroxide), P&T, SVE	PCE concentrations in groundwater reported to range from ND to 3 µg/L	Yes	No

(continued)

Table 2.1. (continued)

Site Name, Location	NAPL Type	Regulatory Oversight Program	Site COCs and RAOs for Groundwater	Technologies Applied	Reported Results	MCLs Achieved?	ICs in Place?
Naval Submarine Base Kings Bay Site 11, Camden County, Georgia	Chlorinated solvents	RCRA Corrective Action	COCs: PCE (8,500 µg/L) TCE (550 µg/L) <i>cis</i> -DCE (1,300 µg/L) Vinyl chloride (4,500 µg/L) RAOs: Reduce groundwater concentration to below Georgia MCLs	P&T, ISCO (Fenton's Reagent), biostimulation, MNA	Concentrations of chlorinated hydrocarbons decreased to 13.9 µg/L; MNA implemented as a final remedy	No	N/A – Awaiting status of MNA
Former Sta-Lube Site, Rancho Dominguez, California	Chlorinated solvents	California Regional Water Quality Control Board, Los Angeles Region	Methylene chloride (2,600,000 µg/L) RAO: Reduce methylene chloride concentration to 50 µg/L	SVE, P&T, excavation, ISCO (catalyzed hydrogen peroxide to activate sodium persulfate)	Methylene chloride levels reduced by 94 to 97% within 4 months following treatment and below the 50 µg/L cleanup goal within 5 months	Yes ^a	No
Pasley Solvents and Chemicals, Inc., Hempstead, New York	Chlorinated solvents	USEPA Superfund	COCs: 1,1-DCA, 1,1-DCE, <i>trans</i> -DCE, chloroform, TCE, toluene, chlorobenzene, ethylbenzene, and xylenes (37,000 µg/L total VOCs, 320 µg/L TCE) RAOs: Reduce concentrations to residential risk levels and MCLs	SVE, air sparging	Concentrations of total VOCs in monitoring wells ranged from ND to 4 µg/L, below MCLs	Yes	No

Notes: µg/L microgram(s) per liter, 1,1-DCA 1,1-dichloroethane, 1,1-DCE 1,1-dichloroethene, *cis*-DCE *cis*-dichloroethene, COC compound of concern, DTSC Department for Toxic Substances Control, IC institutional control, ISCO *in situ* chemical oxidation, MGP manufactured gas plant, MNA monitored natural attenuation, ND non-detect, P&T pump-and-treat, PCE perchloroethene, PCP pentachlorophenol, pg/L picogram(s) per liter, RAOs remedial action objectives, RCRA Resource Conservation and Recovery Act, SVE soil vapor extraction, TCDD 2,3,7,8-tetrachlorodibenzo-p-dioxin, TCE trichloroethene, TPH total petroleum hydrocarbon, *trans*-DCE *trans*-dichloroethene, VOC volatile organic compound

^aAlthough described as achieving MCLs in the report, methylene chloride concentrations were above the MCL when groundwater monitoring was discontinued

groundwater does not restore the aquifer, limits reuse of the site, and requires that both long-term institutional controls and assurances of sufficient financial resources to maintain these controls must be in place. Stakeholder concerns over the long-term stability of these engineering and/or institutional controls, coupled with issues related to natural resource damage claims when drinking water sources are contaminated, and litigation risks due to property damage or trespass, continue to provide a powerful incentive to responsible parties for improving the capabilities of technologies to remove or destroy DNAPLs in source zones.

Several obstacles have prevented widespread application of source zone depletion technologies. These include:

- Setting functional RAOs (such as achieving MCLs in the source zone) that are likely to be technically impractical at a substantial number of sites (NRC, 2005)
- Uncertainty regarding the long-term effectiveness and cost of source depletion options and the length of time required to achieve RAOs
- Limited number of well-documented case studies that could reduce the uncertainties regarding the likely effectiveness of source depletion technologies

An additional obstacle is the current limited availability of cost cap insurance policies to protect contractors from financial losses in the event of cost overruns for source removal remedies contracted under fixed price arrangements.

An additional uncertainty at many sites is the fraction of the contaminant mass in the DNAPL source zone (and downgradient) that may be present in diffusion-controlled, low-permeability zones inaccessible to fluid flushing technologies (Parker et al., 1996; Liu and Ball, 2002; AFCEE, 2007). In some geological settings, DNAPL constituents will diffuse into these zones relatively quickly due to very high concentration gradients, but these same constituents will diffuse more slowly out of these zones after the DNAPL has been removed as the concentration gradients will be significantly reduced. If the metric for successful remediation is achievement of MCLs, the source depletion goal must include depletion of the dissolved- and sorbed-phase mass in addition to the DNAPL mass, which may be significant depending on the amount, type and age of the DNAPL release in the source area as well as matrix characteristics such as effective porosity. *In situ* technologies for source zone depletion are generally limited in their ability to remove contaminant mass from these low-permeability zones; however, thermal technologies may overcome this limitation at some sites. Conversely, it is likely that continued release of contaminants from these low-permeability zones will be at mass discharge rates substantially lower than those prior to source depletion (Sale et al., 2008a). Whether this reduction in source zone mass discharge will be sufficient to warrant implementation of a source depletion technology is not currently predictable and remains an important research topic.

2.3 PERFORMANCE PREDICTION LIMITATIONS

Modeling codes and decision tools are available to (1) predict the performance of DNAPL source zone remediation technologies, (2) predict the beneficial and adverse impacts after remediation has been attempted and (3) guide the decision process for selecting technologies or to achieve desired end points. However, the reliability of the output from these codes and tools is largely a function of the quality of the input. Given the difficulty in accurately characterizing the geology, hydrogeology and contaminant distribution at a particular site, it follows that predictions of remediation technology performance are typically associated with significant uncertainty. Consequently, DNAPL models primarily are used in a conceptual mode. Modeling codes and decision tools are discussed in Chapters 5 and 6 of this book.

Much of the difficulty in quantifying treatment benefit results from the inherent uncertainty in determining the magnitude and distribution of the DNAPL source zone mass prior to remediation. Uncertainties in predicting remedial performance, life cycle costs, and benefits further confound both economic and technical analyses and comparisons of technical options for DNAPL source zone depletion. For example, the use of traditional economic analyses to compare alternatives that require different time frames to achieve remedial goals is meaningless when the time of remediation exceeds about 50 years using standard Office of Management and Budget (OMB)-defined net discount rates. Typical net discount rates used in such comparisons range from 3 to 7%. Unless the discount rate is set to zero (no discounting of future expenditures), net present value of costs in the future (in particular greater than 50 years from the present) will approach zero.

One likely strategy for achieving benefits through partial source mass depletion is to reduce contaminant mass discharge to a level less than the natural attenuation capacity of an aquifer with respect to the dissolved plume. Under such conditions, the contaminant mass discharge for the DNAPL constituents becomes less than the rate of contaminant degradation in the plume, and as a result the plume gradually shrinks until a smaller steady-state plume is achieved. Such a strategy is most likely to be beneficial for small DNAPL source zones at sites that are inactive. However, at many chlorinated solvent sites, natural attenuation by abiotic or microbial degradation may be of insufficient magnitude because of inadequate microbial densities and non-optimum geochemical conditions in the plume. Modifications of these conditions will often be necessary to achieve acceptable degradation rates to be protective of potential receptors.

The following section summarizes the current state of the practice with respect to management of DNAPL sites, focusing on site characterization and remediation.

2.4 SOURCE CHARACTERIZATION AND MONITORING

The challenges involved in characterizing DNAPL sources are daunting. DNAPL migration pathways are governed by even slight differences in permeability and often occur over relatively large areas compared to the original release points. Thin accumulations can be difficult to detect, and contaminants that later sorb and/or diffuse into the aquifer materials are difficult to find. To help the reader appreciate the issues involved, the following sections provide a brief overview of DNAPL sites and their evolution over time, a summary of the source characterization challenges, and a description of the conventional and more innovative tools that can be useful in dealing with these challenges.

2.4.1 Overview of a DNAPL Site

DNAPLs represent continuing, long-term sources of dissolved constituents to groundwater. Although DNAPL compounds generally have low aqueous solubilities (less than 10,000 milligrams per liter [mg/L]), they are orders of magnitude greater than the relevant health-based cleanup levels, which are in the low parts per billion (ppb) range for chlorinated solvents (Pankow and Cherry, 1996). Consequently, it is common for a dissolved or an aqueous plume at concentrations above regulatory limits to develop downgradient of the DNAPL. Therefore, a DNAPL-impacted site consists of a DNAPL zone and a plume emanating from the source area. DNAPL-impacted sites can vary significantly in size, from small (dry cleaners) to very large (the Motorola 52nd Street Superfund site, including additional downgradient sources and similar sites with plumes extending for several miles downgradient). The challenges associated with characterizing and remediating DNAPL-impacted sites will vary with the

size and complexity of the sites, along with evaluating the potential benefits of corrective remedial actions.

The DNAPL zone can include one or more of the following long-term, continuing sources of constituents of concern to the aqueous plume:

- Residual DNAPL (ganglia)
- Pooled DNAPL
- Sorbed constituents
- Dissolved constituents in the pore water or diffused into fine-grained media

Residual DNAPL comprises isolated blobs and ganglia of organic liquid trapped by capillary pressure. Residual DNAPL is formed at the trailing end of a migrating DNAPL body and typically occurs at saturations of no more than approximately 25% of pore space (Kueper et al., 1993). Pooled DNAPL represents a continuous accumulation of organic liquid above a capillary barrier such as a layer of silt, fine sand, or clay. DNAPL saturations within pools are typically between approximately 25 and 80% of pore space. Depending on the stratigraphy, the source zone may contain a complex distribution of residual and pooled DNAPL that is difficult to locate and characterize. This was demonstrated by Kueper and co-workers (Kueper et al., 1993; Poulsen and Kueper, 1992) at a field site located at Canadian Forces Base Borden, where perchloroethene (PCE) DNAPL was released into a sand aquifer both above and below the water table. The resulting pathways and complex distribution of residual and pooled DNAPL were found to be governed by small-scale porous media structure at the scale of millimeters.

Both residual and pooled DNAPL will dissolve into flowing groundwater giving rise to aqueous-phase plumes of dissolved contamination. Pooled DNAPL has less contact with flowing groundwater than does residual DNAPL given the relative differences in the DNAPL-specific surface area exposed to the groundwater. In addition, pools contain DNAPL at higher saturations than zones of residual DNAPL. Consequently, the rate of dissolution is low in pools compared to residual DNAPL, and the DNAPL lifetime in pools will generally be much longer. At most sites, the DNAPL was released decades ago, and in many of these older sources, only pools will remain. For DNAPL sites without pools, it is possible that residual DNAPL has been eliminated by dissolution and no longer represents a source; in fact, the aqueous plume may be detached from the source zone (Sale et al., 2008a).

At older sites, significant transfer of dissolved constituents into fine-grained media via diffusion may have occurred, depending on the site geology. At sites where sufficient sorption and diffusion have occurred, back diffusion of constituents is a continuing source to the aqueous plume and can occur in both the DNAPL zone and within the aqueous plume where fine-grained media exists (Parker et al., 1996; Liu and Ball, 2002; AFCEE, 2007). Finally, desorption of constituents is another phenomenon contributing DNAPL constituents to the aqueous plume.

A life cycle refers to all the stages of a process or a site from beginning to end. Once the components of a life cycle of a particular process are determined, a life cycle analysis (LCA) can be conducted to examine all major steps along the way in terms of environmental, societal, and economic concerns. Ideally, alternatives at each step are evaluated in terms of risks, energy and material usage, costs and benefits, and an optimal approach is determined. The focus of the following section is the major components of the “life cycle of a DNAPL site investigation and remedy.” This differs from the “life cycle of a source zone” as discussed and illustrated in Chapters 1 and 13 of this book, which focus on the aging of DNAPL source zones and changes in transfer of mass with time.

2.4.2 Life Cycle of a DNAPL Site Investigation and Remedy

The life cycle of a DNAPL site investigation and remedy can include the following: (1) contamination discovery and reporting, (2) regulatory decision (resource allocation), (3) decision on investigation strategy based on the initial Conceptual Site Model (CSM), (4) dissolved plume characterization (often performed in phases), (5) determining location of the source or the sources, (6) characterizing the source or the sources (often performed in phases), (7) determining that one or more sources is a DNAPL, (8) characterizing DNAPL sources if possible, (9) performing health and environmental risk assessment, (10) establishing remedial action objectives, performance measures and points of compliance, (11) defining an acceptable time frame for restoration, (12) performing a remedy assessment and selecting the remedy, (13) designing the remedy which could include multiple components, (14) constructing the remedy, (15) performance assessment – monitoring remedy impacts and tracking performance measures, (16) optimizing and enhancing the remedy if necessary, (17) LTM, (18) pursuing a TI waiver or other alternative endpoint consideration, and (19) closure. During each of these steps, regulatory approval is generally required, adding to the life cycle time frame. In addition, supplemental characterization, updates to the CSM, remedy optimization and remedy enhancements and modifications can occur throughout remedial design and implementation phases. Thus, life cycle evaluation for a DNAPL site is rarely a linear process.

In general, for Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) NPL sites, the remedy selection criteria that must be considered are outlined in the National Contingency Plan (NCP): overall protection of human health and the environment, compliance with ARARs, long-term effectiveness and permanence, reduction of toxicity, mobility or volume, short-term effectiveness, implementability, cost, state acceptance, and community acceptance. Other potential factors in remedy selection include residuals and by-product formation/control, process and mechanical reliability, ease of operation/control/implementation, and permitting and sustainability metrics (remedy carbon footprint).

At CERCLA and other sites, when groundwater is considered a potential source of drinking water, ARARs will include MCLs for any chemical regulated under the Safe Drinking Water Act as the RAOs throughout the impacted aquifer. As discussed previously, MCLs can be difficult to achieve at sites containing DNAPL. If at some point in the life cycle of a DNAPL site it is determined that ARARs cannot be met in a reasonable time frame, the NCP allows for ARAR waivers (technical impracticability waivers under CERCLA and RCRA) if it can be demonstrated that the standard cannot be met for a specified area or zone of the site. Under this scenario, a zone of the site must be established within which the ARAR will be waived. At non-Superfund sites, other options that have been considered to address this problem include alternative points of compliance and implicit acceptance of long time frames (greater than 100 years) to reach remedy objectives (ESTCP, 2011). The USEPA-recommended process for restoring contaminated groundwater at Superfund sites is summarized in Figure 2.2.

2.4.3 Characterization and Monitoring Challenges

Locating DNAPL source zones can be difficult, especially if the DNAPL is distributed in complex patterns due to multiple release points and subsurface heterogeneities (USEPA, 1992). Under these conditions, direct observation of DNAPL may not be possible. Further, heterogeneities, including fractures, can produce changes in soil/rock concentrations that vary by orders of magnitude over short distances. Kueper and Davies (2009) present a converging-lines-of-evidence approach to assessing the likelihood of DNAPL presence at a site as well as an approach to delineating the spatial extent of the DNAPL source zone.

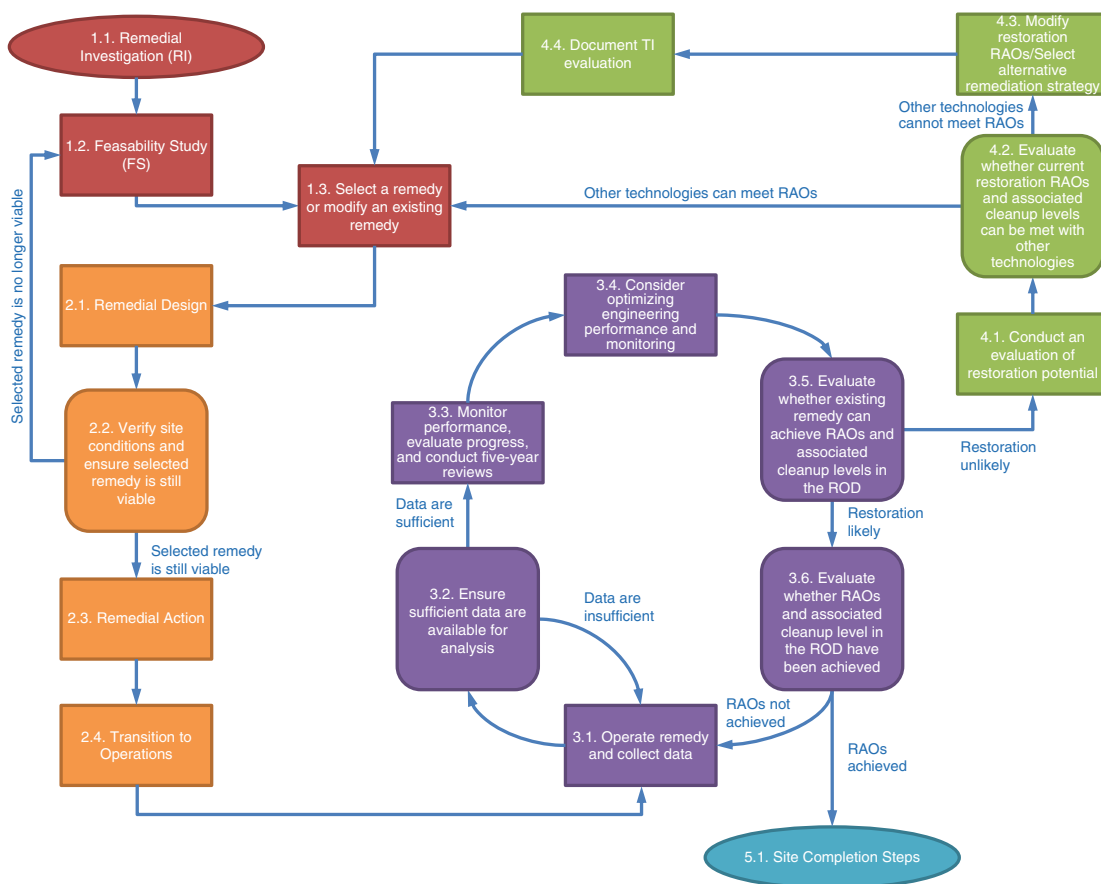


Figure 2.2. USEPA-recommended process for restoring contaminated groundwater at Superfund sites (from USEPA, 2011b). Note: ROD - Record of Decision.

Even if the general area of the DNAPL source zone can be estimated, detailed characterization of the DNAPL extent and distribution is often challenging and inadequate (USEPA, 1992; Cohen and Mercer, 1993). Another difficulty in DNAPL source zone characterization is minimization of the potential for causing cross contamination, especially to deeper stratigraphic layers. The potential for cross contamination is low for smaller, older releases due to matrix diffusion and depletion of the DNAPL caused by dissolution into the aqueous phase as discussed earlier. For more recent and/or larger releases of chlorinated solvents, the potential for cross contamination is high.

To minimize cross contamination, USEPA (1992) suggested an outside-in approach to DNAPL source zone characterization. Even with improved characterization tools such as aquifer profiling using multiple depth-discrete sampling, the outside-in approach is generally preferable. This approach, in which data are first collected downgradient of the source zone, allows better definition of stratigraphy and back tracking to depth-discrete, pooled and residual DNAPL. This information often can be used to improve the later detailed source zone characterization (Mercer et al., 2010).

Another challenge associated with characterizing a DNAPL source zone is measuring the impacts of mass removal on the flux of contaminants from the source. Typically, site-specific cleanup standards consist of chemical-specific concentrations, often MCLs. These concentrations are often in the very low ppb and are rarely, if ever, achieved in and immediately downgradient

of a DNAPL source zone. Consequently, as a practical matter (and not necessarily a regulatory opinion), mass flux measurements and mass discharge estimates have been suggested as alternative performance measures, requiring nontraditional characterization techniques to measure mass flux and discharge before and after remediation (Kavanaugh et al., 2003; ITRC, 2010).

Since some DNAPL is likely to remain in place following remedy implementation, post-remedy site characterization also typically involves LTM, which is used to evaluate the degree to which the remedial measure achieves its objectives (USEPA, 2012). LTM is a significant, persistent and growing cost in remediation at sites relying on containment. Consequently, efforts are being made to optimize LTM and reduce long-term costs. This optimization may take the form of reduced samples in time and space based on statistical evaluation of the number and location of wells necessary to monitor a plume (AFCEE, 2006) and/or more efficient sampling (sensor systems or diffusion samplers).

2.4.4 Conventional Methods

Given the complexity and cost of DNAPL site characterization, it is critical to use a dynamic and flexible approach based on a CSM that optimizes characterization over time (Mercer et al., 2010; USEPA, 2011a). The CSM forms the basis for designing a data collection program, which is phased using an outside-in approach and may initially rely on noninvasive and minimally invasive methods such as soil, gas, and surface sampling prior to drilling or subsurface probing. Stratigraphic information can help identify preferential pathways and traps for DNAPL. Dissolved concentrations in groundwater, which is an integrator of contamination and can be used to more easily find potential DNAPL source contamination than point soil samples, can be used along with site history information to trace back to likely DNAPL source zones.

Conventional methods relied largely on groundwater monitoring wells. For deeper contamination and for stratigraphy (consolidated layers) where direct-push technologies cannot be utilized, monitoring wells are still required. Primary limitations associated with monitoring wells include the possibility of drilling through a DNAPL zone and not identifying it and a general lack of vertical contamination distribution delineation. Vertical delineation is aided by the use of well clusters screened at different depths and use of multi-level sampling systems within a single well (Einarson and Cherry, 2002). Other conventional methods include soil gas surveys, surface geophysics and soil/rock core sampling. These techniques may be helpful in locating potential DNAPL source areas and/or stratigraphy that may serve as DNAPL traps, but the information they provide may not allow determination of the structure and quantity of DNAPL. Figure 2.3 illustrates an example estimated DNAPL distribution for Launch Complex 34 Solid Waste Management Unit (SWMU) Number CC054 based on interpolation of 1,200 soil samples collected from 90 discrete boring locations.

2.4.5 Innovative Methods

Although sampling technologies for soil characterization are mature, innovations for soil characterization include the use of equilibrium partitioning calculation and soil chemistry combined with graphical methods to determine DNAPL source structure and quantity. Innovative techniques for DNAPL characterization in groundwater include improvements in direct-push technology and sensors. Kram et al. (2002) compared several DNAPL characterization methods and concluded that direct-push sensors (cone penetrometer testing, laser-induced fluorescence, and membrane interface probes) and the down-hole NAPL FLUTe™ liner methods are particularly cost-effective components of integrated DNAPL site characterization.

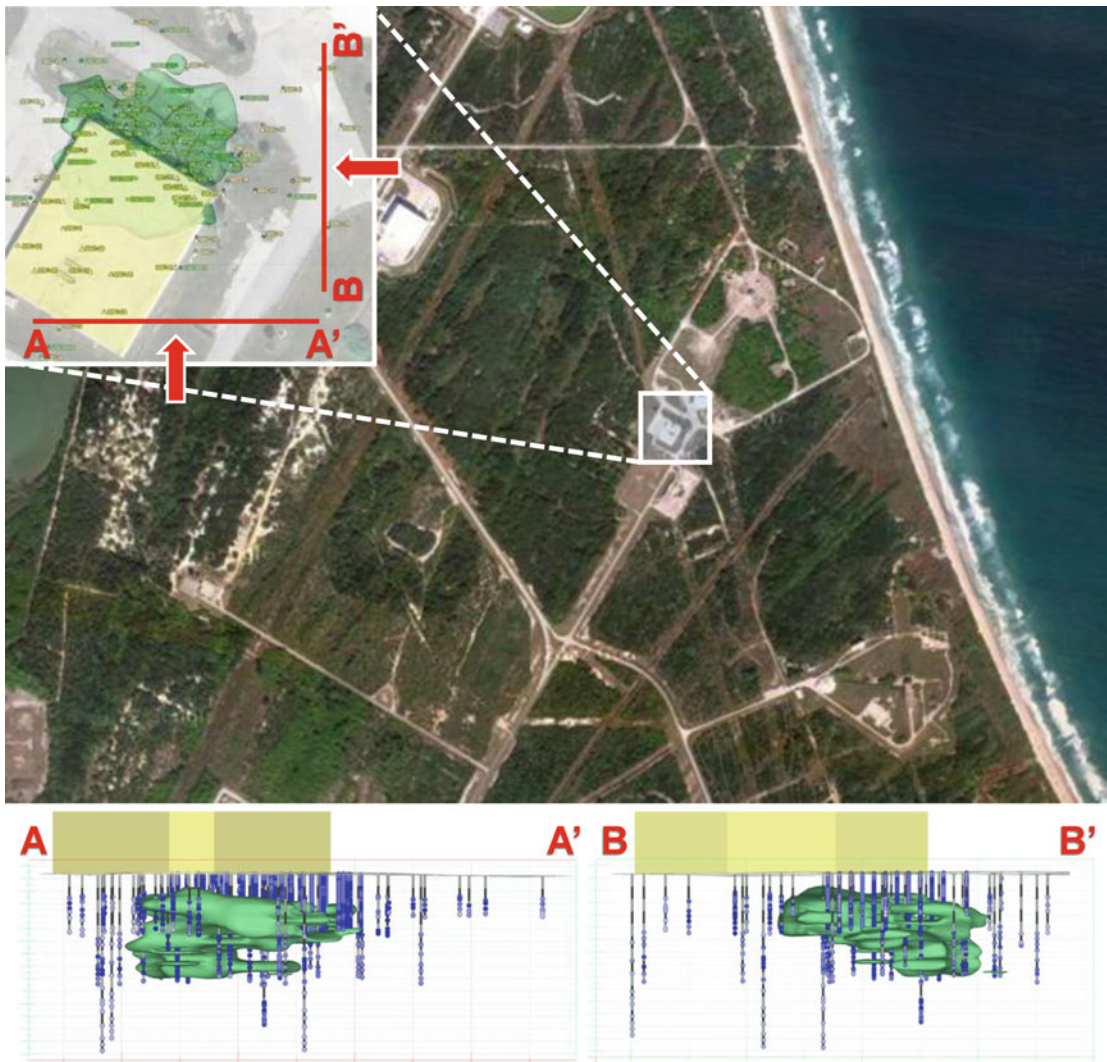


Figure 2.3. Estimated DNAPL distribution at Launch Complex 34 SWMU No. CC054 based on interpolation of 1,200 soil samples collected from 90 discrete boring locations (from Geosyntec and Tetra Tech 2007).

These methods are useful in shallow (less than 100 ft [30 m] below ground surface) subsurface environments that are accessible using direct-push technologies.

As mentioned, mass flux and discharge measurements are used to assess DNAPL impacts to groundwater. They also provide estimates of DNAPL source strength and mass loading. Mass flux and discharge can also be used as metrics to assess the impact of source remediation and are a key input to evaluate monitored natural attenuation. Methods to measure mass flux include using (Mercer et al., 2010) (1) water quality data from transects (multiple locations and depths) and groundwater velocity, (2) sorptive permeable media in downgradient wells to intercept contaminated groundwater and release resident tracers (the passive flux meter method), and (3) plume capture by pumping (the integral pumping method). An advantage of using the transect method is that data may be helpful in backtracking up gradient, following the location of the highest concentrations to identify depth-specific DNAPL source locations. The strengths and limitations of the flux measurement methods are evaluated in a recent ITRC (2010) report.

2.5 REMEDIATION TECHNOLOGIES

A number of technologies have been or are currently being applied to address DNAPL in the subsurface. The performance and limitations of many of these remedial technologies are discussed by Stroo et al. (2012) and are summarized below. The most effective approach to remediating DNAPL sites may be strategic combinations of two or more of these techniques, often starting with high energy approaches and polishing with more passive methods.

Remediation technologies have been described in detail in various documents (ITRC, 2004, 2005a, b; USEPA, 2004; 2006), and individual technologies are discussed in various chapters of this book. All technologies currently considered viable for DNAPL source treatment have specific strengths and limitations. The following presents a brief synopsis of the current state of the practice understanding of the technologies most applicable to DNAPL source depletion.

2.5.1 Hydraulic Displacement

Hydraulic displacement involves the recovery of pooled DNAPL by pumping from either vertical wells or horizontal drains. The rate of DNAPL recovery can be enhanced by water injection, which produces a favorable alteration of capillary pressures (Gerhard et al., 2001, 1998; Alexandra et al., 2012). This technology is best suited to sites containing appreciable amounts of pooled DNAPL. The technology does not remove residual DNAPL and therefore removal is limited by the amount of DNAPL mass present in pools. Hydraulic displacement can be viewed as a source zone stabilization technology in that pooled DNAPL is removed and it is often used as an initial means of DNAPL mass removal, followed by a mass transfer-based technology.

2.5.2 *In Situ* Chemical Oxidation

In situ chemical oxidation (ISCO) can be applied to treat DNAPL sources, particularly if the contaminants of concern are chlorinated ethenes. Technology practice guidance documents for ISCO have been developed and are widely available (Siegrist et al., 2011). ISCO is an attractive technology because it can destroy contaminants rapidly *in situ*, at moderate cost. However, the technology has a number of significant limitations related to oxidant delivery and concentration rebound following treatment (McGuire et al., 2006; Krembs et al., 2010). The most commonly used oxidants include catalyzed hydrogen peroxide (CHP) and permanganate (Krembs et al., 2010), although work to develop improved ISCO formulations is ongoing. In particular, use of activated persulfate is increasing because it is relatively stable in the subsurface compared to CHP and is capable of treating a wide variety of contaminants (Watts and Teel, 2006; Waldemer et al., 2007).

Other research has focused on improving hydrogen peroxide application through the use of stabilizing agents (Watts and Teel, 2006) and permanganate application through the use of agents to control formation of manganese dioxide (MnO₂) particles (Smith et al., 2008). Work to evaluate ISCO in combination with other source depletion technologies suggests that ISCO can be compatible with other technologies such as *in situ* bioremediation (ISB) (ESTCP, 2010) and thermal treatment (Pennell et al., 2009), provided that the secondary effects of ISCO such as oxidation of natural organic material and metals are managed.

2.5.3 *In Situ* Chemical Reduction

In situ chemical reduction (ISCR) is a proven technology for treating groundwater plumes, typically as zero-valent iron (ZVI)-permeable reactive barriers (Gillham and Vogan, 2010).

However, effective delivery of micron-sized ZVI within source areas is difficult, and recent work has focused on alternative delivery mechanisms such as large-auger subsurface mixing (Wadley et al., 2005) and injection of nanoscale ZVI (Gavaskar et al., 2004). Research to improve nanoscale ZVI surface properties and thereby improve delivery within the subsurface is ongoing. The major problems include particle agglomeration and inadequate penetration of the nanoscale ZVI into the formation (Saleh et al., 2007; Berge and Ramsburg, 2009). ISCR can be used in conjunction with other source depletion technologies, particularly ISB, where the addition of ZVI may make the subsurface amenable to subsequent anaerobic biodegradation (Gavaskar et al., 2004), and materials that combine ZVI with electron donors are commercially available. In spite of advances in material formulation and delivery, however, ZVI appears to be more appropriate as a source containment technology (Taghavy et al., 2010).

2.5.4 Surfactant and Cosolvent Flushing

In recent years little work has focused on enhanced flushing with surfactants and/or cosolvents. These technologies can be effective, although, as with any flushing technology, contaminants are preferentially removed from transmissive zones but can be unaffected when present in hydraulically inaccessible zones (Childs et al., 2006; Ramsburg et al., 2005). In addition, chemical costs for some surfactant formulations can be high relative to other technologies (Fountain et al., 1996). Most recent work has instead focused on coupling surfactants and cosolvents with other source treatment technologies such as ISCO to improve distribution during delivery (Dugan et al., 2010).

2.5.5 *In Situ* Bioremediation

In the past several years, ISB has been recognized as a potentially effective treatment of DNAPL sources (ITRC, 2005b). While not appropriate for all DNAPL sources (ITRC, 2008), case study reviews have indicated that in some cases ISB can be as effective as other source remediation technologies (McGuire et al., 2006). In particular, ISB may enhance dissolution rates from residual DNAPL during treatment, with dissolution enhancement factors (compared to natural dissolution) between two and five reported (Sleep et al., 2006; Amos et al., 2008). ISB treatment may be relatively long lasting, with sustained treatment for several years, and can be optimized through the use of bioaugmentation cultures to reduce treatment lag times and cost (ESTCP, 2005; NAVFAC, 2007).

ISB also may be effective for treating hydraulically inaccessible zones through diffusion of slow-release electron donors such as vegetable oil into less permeable materials, although work to demonstrate degradation in these less permeable materials is ongoing as part of ESTCP project ER-1740. Some secondary effects, notably pH decreases, methane production, and increases in dissolved iron and arsenic concentrations have been observed during implementation of ISB source zone remedies, but such impacts are typically localized to the treatment area (ITRC, 2008). Finally, ISB is also attractive as a potential combined remedy (or polishing treatment) for other source treatment technologies such as ISCO (ESTCP, 2010), surfactant flushing (Ramsburg et al., 2004) and *in situ* thermal treatment (Costanza et al., 2009).

2.5.6 Natural Attenuation of Sources

Natural attenuation is defined as any combination 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”

(Wiedemeier et al., 1998). These processes include advection, dispersion, adsorption, volatilization, and chemical or biological stabilization, transformation, or destruction of contaminants. Monitoring to evaluate whether these natural attenuation processes are ongoing as expected is referred to as MNA. For sites where an integrated approach to source management is applied (source mass depletion combined with less aggressive approaches for managing the dissolved plume), natural attenuation may be a viable approach, even in the presence of DNAPL (Rao et al., 2001; ITRC, 2002). However, this approach requires that an MNA remedy will achieve remedial objectives within a reasonable time frame and in some cases may require removal or isolation of a DNAPL source (USEPA, 1998). Further discussion of source zone natural attenuation and use of source zone monitored natural attenuation as a remedy component is provided in Chapter 13 of this book.

2.5.7 *In Situ* Thermal Treatment

Thermal treatment can be highly effective with respect to source zone mass depletion with mass removal in excess of 99% possible even in heavily contaminated sources (Johnson et al., 2009). In addition, it may be particularly attractive for source zones characterized by significant amounts of low-permeability media, where flushing technologies may be less effective. However, mass removal may be incomplete within the low-permeability zones, and effectiveness may be limited in zones where groundwater flow is sufficiently fast to reduce the effect of subsurface heating (Costanza and Pennell, 2007). Recent research indicates that thermal treatment may be compatible with ISB if low-temperature treatment is applied (Costanza et al., 2009) or if sufficient time is allowed for microbial species to recolonize the subsurface after treatment (Beyke and Powell, 2005). Work to evaluate thermal treatment as a combined remedy with ISCR is also ongoing (Siegrist et al., 2011).

The most significant limitation of thermal treatment is generally a higher unit cost compared to other technologies, with reported costs for treatment ranging from \$88 to \$300 per cubic yard (McDade et al., 2005). Other challenges include maintaining hydraulic control during treatment and keeping adequate heating within subsurface saturated zones with higher water fluxes entering the heating zone. It should also be noted that thermal remedies are subject to the same limitations of all source zone remedial strategies if the DNAPL source zone is incompletely defined. However, when life cycle costs are considered, the cost of thermal treatment may compare well with other remedial strategies. In particular, the impact of aggressive source depletion using thermal technologies on post-remedy mass discharge from source zones should be carefully evaluated.

2.6 SOURCE REMEDIATION ISSUES

2.6.1 DNAPL Remediation Effectiveness

As discussed here and in previous documents (Kavanaugh et al., 2003), and despite the advances in source treatment technologies described above, remediation is unlikely to achieve cleanup to MCLs in the source zone at a significant fraction of complex sites impacted with DNAPLs. However, DNAPL source remediation can significantly reduce groundwater concentrations of the DNAPL constituents and can remove substantial amounts of DNAPL mass from the subsurface (source depletion). DNAPL mass removal is considered substantial when it would result in a meaningful reduction in mass discharge from the source zone and/or a reduction in the length of time to reach site closure or other final management stages of a site, such as LTM. The amount of DNAPL mass removal required for meaningful reductions in

mass discharge and time to closure will vary between sites and depends on numerous factors such as site hydrogeology, DNAPL release history and distribution in the subsurface, uncertainties in estimating DNAPL mass present in the subsurface, and potential problems related to remediation of dissolved-phase plumes downgradient of a DNAPL source due to diffusional phenomena.

Select pilot- and full-scale implementations of DNAPL source remediation were evaluated by Kavanaugh et al. (2003). The case studies indicated that substantial (greater than 50%) DNAPL mass removal could be achieved, with corresponding significant decreases in contaminant concentration in groundwater. It should be noted that none of the implementations evaluated achieved MCLs at the time of the study. Other case study evaluations have reported similar remedial performance, with estimated DNAPL mass removals exceeding 90% in some cases (NRC, 2005; ITRC, 2011).

McGuire et al. (2006) evaluated the performance of four DNAPL source depletion technologies (ISCO, ISB, thermal treatment and surfactant/cosolvent flushing) at a total of 59 sites impacted by chlorinated volatile organic compounds. Performance was evaluated on the basis of volatile organic compound (VOC) concentration reduction and rebound, with limited evaluation of alternative performance metrics such as DNAPL mass removal and mass discharge reduction, probably due to limitations in the available data. Evaluation of remedial performance with respect to differences in site hydrogeology was also limited. Median concentration reductions for the four technologies exceeded 80%; however, the concentration reductions varied significantly. For 11 of the 59 sites where DNAPL mass removal could be estimated, the relationship between aqueous concentration reduction and mass removal was within 30% of a 1:1 relationship (50% mass removal corresponds to a 50% concentration reduction).

A similar performance evaluation was conducted by Krembs et al. (2010), focusing on the performance of ISCO for sites with and without DNAPL present. Of the 242 sites evaluated, 104 reportedly contained DNAPL. The performance evaluation incorporated site hydrogeology in sorting the case studies following the approach developed by the NRC (2005) along with alternative performance metrics (cleanup levels other than MCLs, mass reduction goals, etc.). No clear differences in ISCO performance as a function of site hydrogeology were observed, although practitioners may vary the implementation approaches for sites with different geological conditions. For sites where DNAPL mass removal data were available, the estimated amount of relative mass removal was greater than the relative concentration reduction (the relationship did not follow a 1:1 ratio). The study also indicated that, while application of ISCO at a DNAPL site is unlikely to achieve MCLs in the source zones, it can achieve alternative remedial objectives such as significant mass removal if realistic expectations of remedy performance are specified.

Johnson et al. (2009) presented a state of the practice overview of *in situ* thermal treatment of DNAPL source zones. Unlike many remedial performance reviews, the overview incorporated information on the hydrogeological settings and where treatment was applied, as well as a variety of performance metrics such as concentration reduction, estimated mass removal and mass discharge. In general, thermal applications were limited in more complex hydrogeologic settings, likely reflecting the risks and uncertainties related to remediation in those environments. Only a small subset of the evaluated applications had sufficient data to allow for an evaluation of mass discharge reductions, reflecting the fact that this important information is seldom collected as part of performance monitoring. Of the applications with sufficient data to perform an evaluation, the mass discharge reduction from the DNAPL source zone ranged over several orders of magnitude, from reductions of less than a factor of 10 to reductions of greater than a factor of 10,000. Only one application in a complex hydrogeology

(fractured bedrock) had sufficient data to perform an evaluation of mass discharge reduction, and in this case the reduction was limited (less than a factor of 10).

When assessing the performance of the remedial technologies used for DNAPL source depletion, both the inherent limitations of a technology and any limitations related to design and operational decisions made by the practitioners implementing the technology will have an impact. For example, a key conclusion of the overview of *in situ* thermal treatment presented by Johnson et al. (2009) is that many treatment systems were designed to remediate a DNAPL source that was smaller than the actual source zone, limiting the effectiveness of the remedy. In these cases, additional characterization work could have resulted in a more complete understanding of the extent of the DNAPL source, thus improving remedy performance. In addition, the operational period of many *in situ* thermal remedies appears to be somewhat arbitrary, with little regard for system optimization or monitoring. Other DNAPL source remedies often have similar practitioner-related limitations, such as determining when to cease amendment injections for ISCO or ISB. The ability to discriminate between technology- and practitioner-related limitations has not been resolved to date. However, in our experience surprises are common and implementation is often less than ideal. As a result, source treatments should be carefully designed and operated to minimize performance issues resulting from the implementation, as opposed to any inherent limitations of the remedial technology.

2.6.2 Technology Applicability

Attempts have been made to evaluate DNAPL mass removal performance in the context of site conditions (ITRC, 2002; Pankow and Cherry, 1996). Kavanaugh et al. (2003) presented a conceptual evaluation of the potential applicability of different technologies for depleting DNAPL mass under two different hydrogeological settings: hydraulically accessible, where permeable zones are connected to wells, and hydraulically inaccessible, where impermeable zones or permeable zones are not connected to wells. The evaluation further considered two different DNAPL loading scenarios: pooled DNAPL in significant mass and DNAPL distributed as residuals with a relatively small total mass. For hydraulically accessible zones, many technologies were considered to be potentially effective for DNAPL mass depletion, particularly for residual DNAPLs with small mass. In contrast, most technologies were not expected to be practical or effective for depletion of DNAPL mass in hydraulically inaccessible zones.

Similarly, a committee organized by the NRC (2005) has developed a multidimensional screening matrix for evaluating potential technology performance based on factors including remedial objectives, remedial technology, and site hydrogeological setting. Five relatively generic hydrogeological setting types are considered in the screening matrix:

- Type I – Granular media with mild heterogeneity and moderate-to-high permeability
- Type II – Granular media with mild heterogeneity and low permeability
- Type III – Granular media with moderate-to-high heterogeneity
- Type IV – Fractured media with low matrix porosity
- Type V – Fractured media with high matrix porosity

For a specific site, the screening matrix can be used to compare the expected efficacy of different DNAPL source depletion technologies. Technologies are compared on the basis of achieving functional goals, such as plume containment, mass or concentration reductions, and risk management rather than absolute objectives such as protection of human health and the environment.

In deciding whether DNAPL source depletion is appropriate for a given site, the key question is how much mass removal can reasonably be achieved and whether this mass removal will be sufficient to meet remedial objectives within the source zone within some reasonable time frame. In addition to the applicability of source depletion technologies, a number of site-specific factors are important when considering whether containment or source depletion may be appropriate. Some key factors include the distribution of contaminants within the source zone, source hydrogeological setting, age of the source, and whether the source area has been sufficiently characterized for the remedial approach selected. It should also be noted that this discussion is focused primarily on remediation and/or containment of the DNAPL source. However, many large DNAPL sites currently have downgradient groundwater plumes that can extend for thousands of feet, and containment in those cases may also refer to remedial efforts to prevent further spread of impacts downgradient of a DNAPL source.

2.6.3 Contaminant Distribution

Contaminants within a DNAPL source zone may occur in four different phases:

1. DNAPL (pooled or residual)
2. Gas in soil vapor
3. Dissolved in groundwater
4. Sorbed on aquifer material

The processes governing distribution of each of these phases within the subsurface have been extensively described in the literature (Feenstra et al., 1996; Falta et al., 1989; Freeze and Cheery, 1979; Sale et al., 2008a; and Schwarzenbach et al., 1993) and are not repeated here. The total mass of contaminant present within a source zone will be equal to the sum of the mass within each of these four phases, with the distribution of mass within the phases varying based on site-specific characterizations. In addition, each of the four phases may occur in hydraulically accessible or inaccessible zones, alternatively described as mobile and immobile pore space (Payne et al., 2008). The distribution of contaminants between these four phases, and particularly the distribution within the immobile and immobile pore space, is a critical factor affecting source treatment performance of any *in situ* technology.

Back diffusion is a process that has been recognized for many years (Parker et al., 1996), but interest has increased in recent years. Back diffusion occurs when the concentration of dissolved-phase contaminants in groundwater within the mobile pore space is greater than the concentration within the immobile pore space, resulting in diffusion of the contaminants into the immobile pore space. Once concentrations within the mobile pore space decrease, contaminants will begin to diffuse from the immobile zones into the mobile pore space. This process is known as back diffusion or matrix diffusion and can result in persistent groundwater plumes, even following depletion of DNAPL that may have been present in the source (Parker et al., 1996; Liu and Ball, 2002; AFCEE, 2007; Sale et al., 2008a; West and Kueper, 2010). Depending on site geology and DNAPL release history, the amount of mass present within the immobile pore space may be significant and represent a long-term secondary source of contamination to the groundwater. Figure 2.4 illustrates the distribution of PCE in the lower aquifer and aquitard at Dover Air Force Base, Delaware, prior to and following groundwater extraction and treatment (Liu and Ball, 2002). The data show that pump-and-treat provided significant concentration reductions in the aquifer but that diffused mass persisted in the aquitard.

Contaminant distribution within each of the four phases described above for a given source is related to the hydrogeological setting. Using the framework of the five geological type

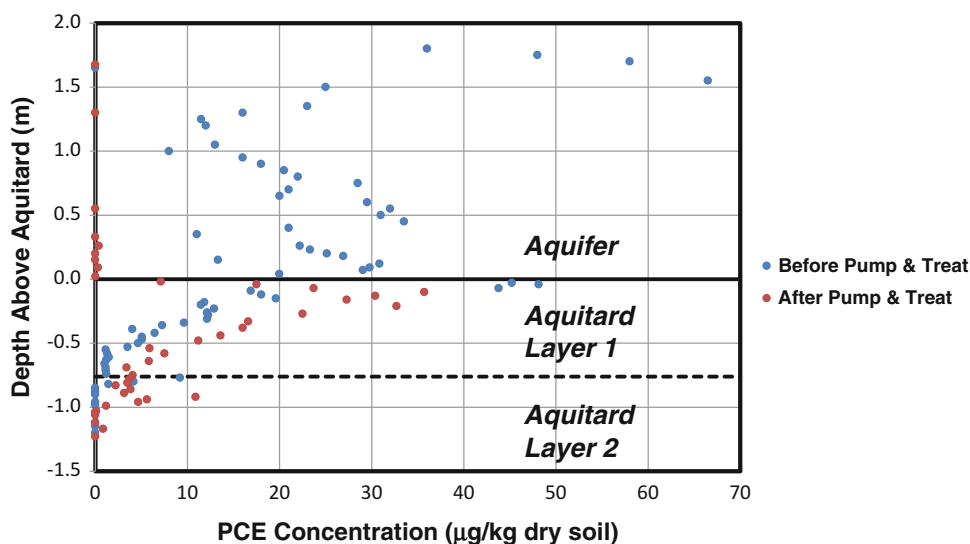


Figure 2.4. PCE in the lower aquifer and aquitard at Dover Air Force Base, Delaware, prior to and following groundwater extraction and treatment (from Liu and Ball, 2002).

settings developed by NRC (2005), contaminant distribution as it relates to hydrogeological setting can be described as follows (Sale and Newell, 2010):

- Type I settings are characterized by granular media with mild heterogeneity and moderate-to-high permeability, resulting in limited contaminant storage within immobile pore space. In this setting, the dominant contaminant storage mechanisms are dissolution from DNAPL and sorption to the aquifer material.
- Type II settings are uncommon but are characterized by granular media with mild heterogeneity and low permeability, resulting in a source that essentially comprises entirely immobile pore space. In this setting the dominant contaminant storage and transport mechanism is diffusion.
- Type III settings are characterized by granular media with moderate-to-high heterogeneity. In these settings, DNAPL constituents will diffuse from the mobile pore space into the immobile pore space. After the DNAPL is depleted, the contaminants present in the immobile pore space will act as a persistent source to groundwater.
- Type IV settings are characterized by fractured media with low matrix porosity. In these settings the primary contaminant storage mechanism is dissolution from DNAPL, with limited mass storage within the low-permeability zones. When the bulk of the DNAPL has dissolved, the plume may persist due to the presence of residual DNAPL in low-flow zones such as dead-end fractures.
- Type V settings are characterized by fractured media with high matrix porosity. In these settings DNAPL constituents will diffuse from the fractures into the porous aquifer material. Once the bulk of DNAPL in the fractures has been depleted, back diffusion from the aquifer material can sustain dissolved contaminant concentrations within the fractures.

In addition to changes in contaminant distribution based on hydrogeology, the age of a source zone will also influence the distribution. Immediately following a release, the contaminants may be present largely as DNAPL, with little or no migration of contaminants into the

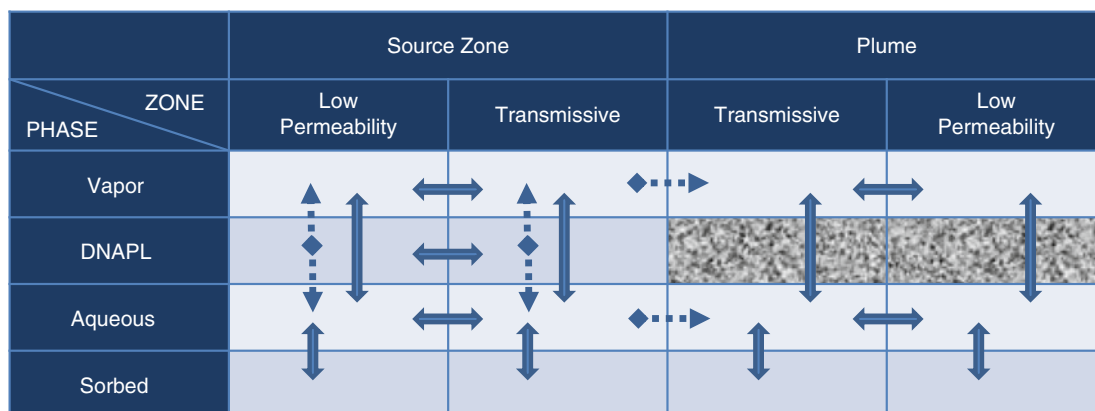


Figure 2.5. Lattice of 17 potentially relevant contaminant fluxes illustrated by the 14-compartment model (from Sale and Newell, 2010).

immobile pore space (life cycle Stages 1 and 2, Chapter 1). As a source zone ages, more of the DNAPL will move into the aqueous, vapor, and sorbed phases and contaminants will be present in the immobile pore space (life cycle Stage 3, Chapter 1). Eventually the source zone will reach the weathered stage where DNAPL has largely been depleted from the more transmissive zones and the groundwater plume is sustained by back diffusion from low-permeability zones located both in the source zone and in the downgradient plume (life cycle Stages 4 and 5, Chapter 1). As discussed, the impact of the back diffusion on groundwater concentrations will vary.

A key ongoing challenge is describing contaminant distribution within a DNAPL source. One approach that has been advanced is an eight-compartment conceptual model to describe the distribution of contaminants within a source zone (Sale et al., 2008a; Sale and Newell, 2010). This model, which is also applied to the plume zone and thus has 14 total compartments, identifies each of the four phases in which organic contaminants can exist and includes separate compartments for mobile and immobile pore spaces. The model incorporates the conceptual mass transfer links between the different compartments. While this model is helpful conceptually, it is difficult to use quantitatively because of the common lack of information on contaminant distribution in all eight compartments, which potentially can be present in more than one hydrostratigraphic zone. Furthermore, the complexity of the model can make it difficult to understand intuitively, particularly for non-practitioners, and to date this approach has not been widely incorporated into decision analysis for source depletion. If data at a particular site are sufficient to quantify the distribution of contaminants using this model, it may become part of a more accurate site-specific CSM, which remains the most effective method for conveying information regarding contaminant distribution within a DNAPL source and downgradient plume. Figure 2.5 illustrates a lattice of 17 potentially relevant contaminant fluxes illustrated by the 14-compartment model (Sale and Newell, 2010).

2.7 BENEFITS OF SOURCE DEPLETION

While some sources may be restored entirely, allowing for unrestricted use and unlimited exposure, in many cases the reasonable expectation is that well-implemented source treatment will reduce mass and concentrations by perhaps 1–2 orders of magnitude, and significant continuing management will be required for many years following active remediation (NRC, 2005; ITRC, 2011). As a result, it often is important to quantify the benefits of partial remediation. To determine how much remediation is needed to allow a transition to passive

treatment or to meet remedial objectives regarding the size or the longevity of the plume, nontraditional metrics such as mass discharge are needed. The following sections discuss the impacts of source depletion on mass discharge and plume behavior to illustrate the opportunities and difficulties associated with considering such alternative criteria for assessing the performance of remedial actions.

2.7.1 Source Depletion and Mass Discharge

The decision to implement a source depletion or containment technology will be influenced by an understanding of where the majority of the contaminant mass in a source zone is located, as governed by source hydrogeology, age, and properties of the DNAPL (Mercer and Cohen, 1993). The complexity of contaminant distribution within a source zone makes *a priori* prediction of reductions in mass discharge or downgradient plume concentrations from remediation efforts difficult. Recent work has focused on evaluating how contaminant distribution within a source impacts remedial performance.

Source architecture is a key feature governing performance of remedial technologies, both in terms of containment mass removal and subsequent impacts to the groundwater plume (Saenton et al., 2002; Fure et al., 2006). The term *source architecture* refers to the distribution of DNAPLs between residual ganglia and pools as well as the distribution of contaminants between mobile and immobile pore space within the source zone (Sale and McWhorter, 2001; Lemke et al., 2004). Source architecture will be a function of the type of DNAPL, DNAPL release history, DNAPL properties, source zone hydrogeology and quantity of DNAPL released cumulatively.

Extensive modeling and laboratory studies have evaluated source zone architecture and associated remedy performance. Sale and McWhorter (2001) modeled dissolution of a heterogeneous DNAPL architecture in a uniform porous media (Type I hydrogeological setting) and observed that contaminant dissolution occurs at the upgradient edge of a DNAPL, implying that contaminant loading to downgradient plumes will continue as long as DNAPL persists. From this observation, Sale and McWhorter (2001) concluded that nearly complete contaminant removal would be required to achieve “significant near-term improvements in groundwater quality,” where a significant improvement was considered to be the several orders-of-magnitude reduction in aqueous concentrations required to achieve risk-based MCLs.

In contrast, Rao and Jawitz (2003) modeled dissolution of a uniform DNAPL within a heterogeneous porous media (Type III hydrogeological setting). Results of their analysis showed that DNAPL mass depletion in the range of 70–90% could achieve 70–98% reductions in contaminant loading to downgradient plumes. Although contaminant reductions of this magnitude may not result in achieving MCLs within a source zone, they may allow for water quality objectives to be met in the downgradient plumes if the reduction in mass discharge results in a stable or a shrinking plume.

Christ et al. (2005) used numerical modeling to evaluate the potential benefits of ISB and surfactant flushing on reducing the longevity of DNAPL sources with varying architecture. The modeled results showed reductions in source longevity regardless of architecture when ISB was applied. However, for sources in which the architecture was dominated by pooled DNAPL the reduction in source longevity was limited, with DNAPL pools present post-remediation sustaining the groundwater plume as long as centuries. For sources with architecture dominated by residual DNAPL (ganglia), ISB and surfactant flushing reduced source longevity to a decade or less theoretically.

In a series of two-dimensional flushing experiments, Suchomel and colleagues (Suchomel and Pennell, 2006; Suchomel et al., 2007) evaluated reductions in contaminant mass discharge

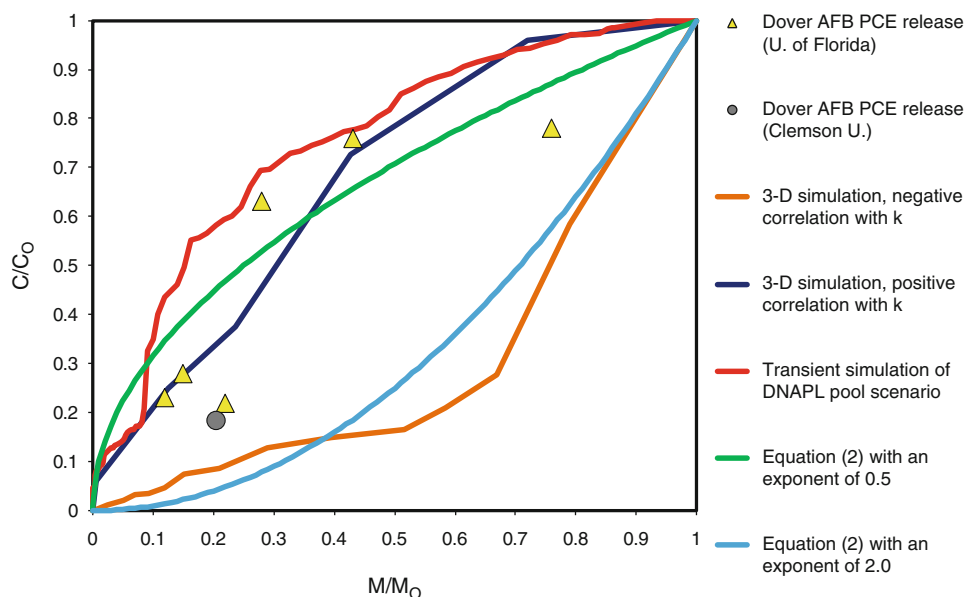


Figure 2.6. Modeled (lines) and observed (points) normalized DNAPL source zone concentrations as a function of normalized source zone mass removal (from Falta et al., 2005a).

following partial source depletion. The experiments were conducted in a Type I hydrogeological setting with DNAPL architectures ranging from pool dominated to ganglia dominated. Results of the experiments indicated that mass discharge can be substantially reduced (40–90%) following partial source depletion (53–85%), consistent with the findings of Rao and Jawitz (2003). Pool-dominated source architectures had the most significant reductions in mass discharge but also had the lowest fraction of total contaminant mass removal and diminishing returns with respect to mass removal efficiency (the mass of contaminant removed per pore volume flushed consistently declined over time). This result is consistent with preferential dissolution of DNAPL ganglia relative to pools and illustrates the trade-off between reducing source longevity and reducing contaminant mass discharge.

Based on these modeling and limited laboratory evaluations, a number of functions have been advanced to describe source architecture and relate source zone mass depletion to down-gradient groundwater quality. Among these are the gamma function (Falta et al., 2005a; 2005b), beta function (Park and Parker, 2008), and ganglia-to-pool ratio, also quantified as the pool fraction (Christ et al., 2005). These functions are useful analytical tools, but determining a representative value for a field site has proven difficult. For example, there has been limited success in locating and quantifying pooled DNAPL with current characterization technologies. Basu et al. (2008) suggested the use of a stream tube model along with partitioning tracer testing to estimate source architecture and predict future source depletion, although attempts to validate this approach in the field have been limited to date. Figure 2.6 illustrates an example of normalized DNAPL source zone concentrations as a function of normalized source zone mass removal (Falta et al., 2005a).

Given the limited ability to estimate source architecture with current characterization technologies, research and fieldwork have focused on relating source architecture and remedial performance to upscaled mass transfer approaches. Park and Parker (2008) developed a model to evaluate the effects of remediation on source mass depletion, mass discharge from a source and downgradient plume attenuation for source architectures dominated by pooled and residual DNAPL. The model results were consistent with approaches that do not incorporate

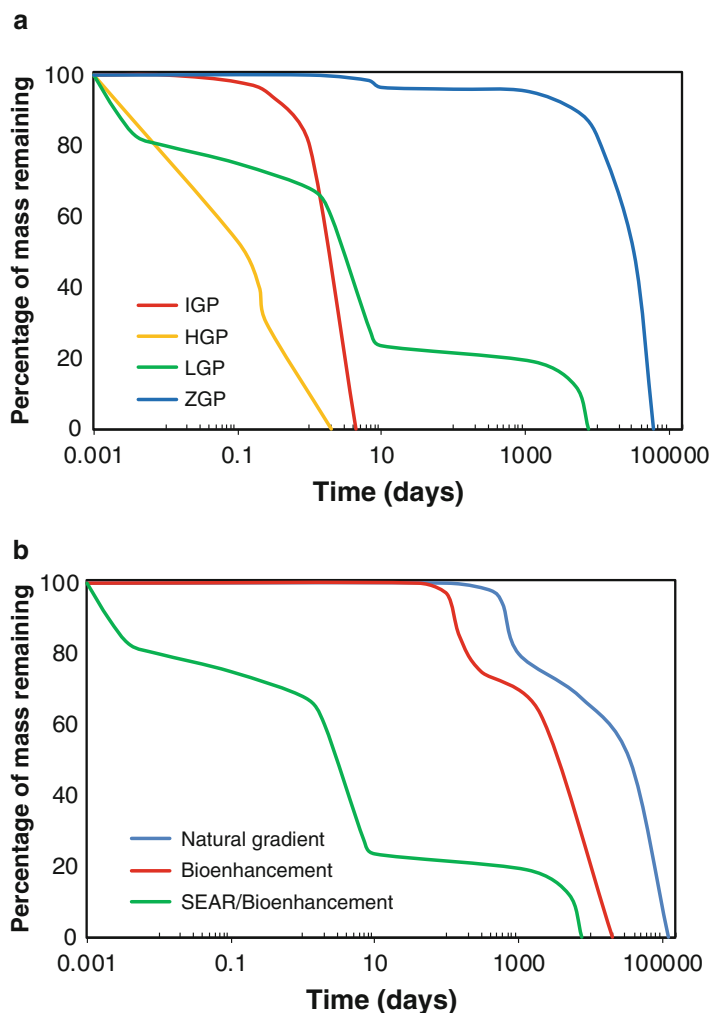


Figure 2.7. Modeled percentage of DNAPL mass remaining as a function of time for (a) surfactant flushing followed by bioremediation for DNAPL distributions ranging from only residual DNAPL (IGP) to only pooled DNAPL (ZGP) and (b) three alternative remediation strategies. The results illustrate the two-stage DNAPL mass recovery that has been observed in the field. From Christ et al. (2005).

upscaled mass transfer coefficients, indicating that partial source depletion reduced source longevity in all cases but that mass discharge reductions were more significant for sources comprising DNAPL ganglia and less significant for pooled DNAPL sources. However, the upscaled mass transfer relationship used by the model to describe dissolution from the DNAPL source was developed by fitting several parameters to time-series mass discharge data, limiting its use as an *a priori* predictive tool.

Christ et al. (2010) refined the approach developed by Park and Parker (2008) to allow estimation of the mass transfer coefficient based only on concentrations at the downgradient boundary of the source and incorporating a function relating beta to the ganglia-to-pool ratio. This refined approach to upscaled mass transfer is useful in that it can simulate the two-stage mass recovery that has been observed in the field (Brusseau et al., 2007) and may occur in

sources that comprise spatially distinct regions of DNAPL ganglia with high contaminant mass discharge and DNAPL pools with lower, but sustained, mass discharge (Figure 2.7).

Research on estimating field-scale upscaled (bulk) mass transfer coefficients based on site-specific data has been conducted as part of ESTCP Project ER-200833. This approach involves relating contaminant mass extraction rates observed during source zone pump-and-treat to the bulk mass transfer rate from DNAPL to groundwater in the source. Bulk mass transfer rates were estimated using this method at a field site impacted by a multicomponent NAPL (jet fuel; benzene, toluene, ethylbenzene, and total xylenes [BTEX]; and naphthalene) before and following a pilot-scale test of thermal enhanced extraction. Observed benzene concentrations in site monitoring wells correlated well to concentrations modeled with the field-scale estimate of the bulk mass transfer rate, indicating that this may be a promising approach for assessing the impact of partial source removal on mass discharge.

In reviewing the work completed to date relating to source depletion, source mass discharge, and source architecture, it must be stressed that this has focused mostly on bench-scale laboratory studies and modeling experiments. The ability to translate this work to the field scale (practicably characterize the gamma function or the pool fraction) has not been demonstrated, and given this limitation, some researchers have questioned the utility of these source characterization metrics (Basu et al., 2008). As a result, current research on source architecture has focused on better predicting plume response to source depletion through groundwater modeling and innovative field characterization technologies such as multi-tracer push-pull testing and measurements of contaminant mass flux (Stroo et al., 2012).

2.7.2 Source Depletion and Plume Behavior

While the current state of the practice suggests that source remediation is unlikely to achieve MCLs in the source zone, benefits to downgradient groundwater quality may nevertheless be realized. Many DNAPL constituents will attenuate naturally in groundwater systems, either through biotic process (Wiedemeier et al., 1998) or abiotic processes (Danielson and Hayes, 2004). As noted earlier, if the rates of these natural attenuation processes are sufficiently rapid, they can result in groundwater plumes that are either stable or shrinking. They may also be sufficient to control contaminants that are back diffusing out of immobile pore space within the groundwater plume.

If the above natural attenuation processes are ongoing at a site, partial source depletion may offer the following benefits:

- For a stable or a shrinking contaminant plume – accelerating the rate at which the plume shrinks and/or decreasing the overall longevity of the plume
- For an expanding contaminant plume – reducing the mass loading to the plume so that the plume may stabilize or begin to shrink

The first of these was illustrated by Chapelle et al. (2004) based on a review of data from a field site in Georgia where source treatment via ISCO was implemented. Following ISCO treatment, concentrations of PCE in the source zone decreased from up to 5,000 micrograms per liter ($\mu\text{g/L}$) to $<100 \mu\text{g/L}$, and a resulting order-of-magnitude concentration reduction was observed in the downgradient groundwater plume. However, natural attenuation of DNAPL constituents at some sites may occur only at very slow rates or not at all. At these sites, relatively little benefit to downgradient groundwater quality may arise from source depletion.

Another potential limitation to the benefit of source depletion on downgradient groundwater quality is the potential presence of contaminants in the immobile pore space within a groundwater plume. Reductions in mass loading due to source depletion/containment may

result in back diffusion of contaminants that may essentially act as a secondary contaminant source within the groundwater plume and sustain the plume for a significant duration, even with source depletion. The impact of back diffusion will vary from site to site and within the same site. Back diffusion sustaining a downgradient plume has been shown at field sites following implementation of source containment technologies (AFCEE, 2007; Sale et al., 2008a).

This phenomenon was explored in detail at a large site in Northern California impacted by chlorinated solvents (Newell et al., 2011). Source areas at the site have been contained either through installation of slurry walls or by source zone pump-and-treat. Mass discharge rates for plume containment pump-and-treat wells at the site were compiled and compared to estimates developed using two analytical models: a simplified advection–dispersion–retardation model and a model incorporating matrix diffusion within the downgradient plume (AFCEE, 2007). In general, the matrix diffusion model better approximated the observed mass discharge at the site, with a normalized root mean square error of 9% for the matrix diffusion model compared to 34% for the advection–dispersion–retardation model. However, inspection of the data indicated that the matrix diffusion model tended to overpredict systematically the amount of mass discharge at a given well, potentially resulting in an overly pessimistic view of plume cleanup.

While the previously described study did not investigate the cause for the overprediction of mass discharge by the matrix diffusion model, the model used was highly simplified. Sale et al. (2008b) have developed an analytical solution to describe matrix diffusion that incorporates other phenomena such as contaminant degradation in both the mobile and immobile pore space and fully models the contaminant distribution within the transmissive zone. This solution may more accurately describe changes in mass discharge due to matrix diffusion, but the highly complex nature of the solution has limited its use to date, although efforts to incorporate it into a practitioner-friendly tool for evaluating matrix diffusion are ongoing.

Given the above examples it is apparent that benefits to downgradient plume concentrations can be realized by source mass depletion, but the extent of the benefits will be highly dependent on the distribution of contaminant mass within the subsurface. The benefits of mass depletion may be related to changes in the natural plume behavior (improved natural attenuation performance) or reductions in plume size due to coupling of active plume remediation with source depletion. A number of researchers are developing screening-level models to assess the potential benefits of source depletion. These include the REMChlor model developed by Falta (2008), an analytical solute transport model, and mass balance-based models developed by Newell and Adamson (2005). Examples of how these models may be used to estimate plume responses to source depletion are discussed in Chapter 6 of this book. However, the currently available screening-level models are limited in some respects, and such limitations need to be considered when using the models for decision-making purposes.

2.8 RISKS OF IMPLEMENTING SOURCE DEPLETION TECHNOLOGIES

The previous sections have discussed the potential benefits related to source depletion, including decreased mass discharge, reductions in downgradient plume concentrations and reductions in remedial time frames. However, negative impacts related to source depletion are also possible. These risks should be considered when making a decision to implement source depletion, with the objective of doing what can be done to improve subsurface conditions weighed against the objective of doing no harm to the subsurface. Specific risks are discussed in detail elsewhere (Kavanaugh et al., 2003) and are summarized below.

- Expansion of a source may occur, particularly when using surfactant flushing or thermal treatment for source depletion (the LC34, Cape Canaveral Air Station, Florida, case study presented in Kavanaugh et al., 2003), with potential contaminant migration into low-permeability media or downward migration into deeper permeable zones.
- Changes to source architecture that reduce the potential for source depletion or increased contaminant mass transfer from DNAPL to groundwater. Such changes could include mobilization of DNAPL ganglia resulting in formation of new DNAPL pools, reducing the efficacy of mass removal technologies. Alternatively, changes to the subsurface permeability distribution due to DNAPL removal could produce transient increases in contaminant flux if the changes to the groundwater flow field result in access to previously inaccessible portions of the DNAPL source.
- Certain source depletion technologies can change the physical characteristics of the source, through formation of mineral precipitates such as manganese dioxide during ISCO, excessive growth of biomass during ISB, or changes to subsurface conditions (localized soil consolidation and/or surface slumping at some sites) related to heating during *in situ* thermal remediation. In many cases, these changes can result in reductions in source permeability, reducing future access to any source material remaining following treatment.
- Similarly, source depletion technologies that rely on injection of chemicals, particularly ISCO and ISB, can also alter geochemical properties of the source, notably pH, oxidation reduction potential (ORP) and salinity. These changes to geochemical properties can limit biological growth and potentially promote the transport of metals with ORP-dependent solubility such as chromium and arsenic.
- Some source depletion technologies (ISCO, *in situ* thermal treatment) may temporarily reduce subsurface biomass, biodiversity and functionality. These impacts appear to be transient in nature, however, and recent research indicates that biological activity can recover following implementation of these technologies.

In addition to the potential risks related to source depletion technologies, other potential negative impacts include an inability to develop or use the site both during and potentially following remediation, financial and/or legal consequences if the target remedial endpoints are not met, and stakeholder concerns if target remedial endpoints are not met and a remedial action is deemed to have “failed.”

2.9 ESTIMATING IMPACTS OF SOURCE DEPLETION ON LIFE CYCLE COSTS

Along with benefits related to mass discharge and concentration reductions, that is, risk management benefits, the potential value of source depletion in the view of the site owner may be in reducing the life cycle cost to achieve cleanup objectives. Annual and life cycle costs for cleanup of sites impacted with DNAPL can be very high. For example, the USEPA 28 Site Study (USEPA, 1999) estimated a median annual cost of \$180,000 (range \$30,000–\$4,000,000) for operation and maintenance (O&M) of pump-and-treat systems for DNAPL source containment. Since many of these containment systems are operating without concurrent implementation of source depletion technologies and may need to operate for centuries to achieve remedial objectives, the life cycle costs are clearly very high in constant dollars.

It is difficult to predict how source depletion will impact life cycle costs given the uncertainties associated with estimating the impacts of partial mass removal on source lifetime

and mass discharge; however, potential economic benefits of complete or partial removal may include the following:

- Earlier site closure when regulatory requirements are met
- Lower annual and life cycle costs due to either reduced O&M costs or creating conditions that allow for implementation of more passive remedial technologies (MNA)
- Removal of liabilities and accrued reserves for remediation
- Enhanced land value due to reductions or removal of residual contamination
- The ability to conduct land transactions that would not be otherwise possible due to land-use restrictions or the need to retain liability and access associated with remedies requiring long-term O&M

While each of the economic benefits listed above could provide cost savings, cost–benefit analyses of potential source depletion remedies are complicated by a number of factors, including differences in accounting practices, discount rates used in analysis and tax consequences of using different remedial technologies (NRC, 1997), and are thus highly site specific. In addition, regulatory drivers specifying restoration goals continue to be the primary reason for remediating DNAPL source zones. Partial source depletion is generally not capable of meeting ARARs, thus limiting the utility of cost–benefit analyses.

The decision to implement source zone depletion technologies at a DNAPL site is based on highly site-specific conditions and criteria, and numerous regulatory, technology and stakeholder factors must be considered. The current decision process, as practiced in the United States, generally has resulted in selection of containment over source depletion. Pump-and-treat and/or MNA, both potential containment technologies, were used as groundwater remedies, either alone or in combination, at 71% of 164 Superfund sites where Records of Decision were issued between 2005 and 2008. During this same time period, institutional controls were included more often than any other groundwater remedy in site decision documents (USEPA, 2010).

2.10 SUMMARY AND FUTURE NEEDS

Several studies over the past decade have concluded that partial mass depletion from DNAPL source zones has been a viable remediation strategy at certain sites and is likely to provide benefits at a number of additional sites (Kavanaugh et al., 2003; NRC, 2005; Stroo et al., 2012). However, barriers to more widespread use of DNAPL source zone technologies persist. Additional theoretical analysis and assessment tools (performance prediction tools, cost–benefit assessment tools, technology failure analysis, reliability of long-term management), improved monitoring techniques for site characterization and performance assessment, and especially field-scale demonstrations that elucidate effective site characterization and technology implementation as well as the benefits of partial source depletion are needed to provide a more informed basis for decision making on whether to undertake DNAPL source zone depletion at both sites with a containment remedy in place and at new DNAPL sites.

This information will also provide a basis to estimate the fraction of DNAPL-impacted sites that would be candidates for implementation of source depletion technologies. At some DNAPL sites, containment may be the only viable remedial option, and at such sites, containment may be considered a “presumptive remedy” eliminating the need for costly additional studies. However, appropriate guidance for defining the conditions under which DNAPL source remediation would be a viable option for site cleanup compared to a containment-only option has not yet been reported. The current strategy of source zone containment has generally proven reliable for limiting routes of human and ecological exposure to chemical

contaminants emanating from DNAPL-impacted sites, provided that the containment system (pump-and-treat or permeable barriers) has been properly designed and maintained. However, this strategy poses long-term risks, transfers the burden of site management to future generations, and requires long-term financial stability of the responsible parties. Furthermore, these long-term risks are generally difficult or impossible to quantify accurately. It is thus imperative that sufficient resources be devoted to resolving the many uncertainties in DNAPL source zone characterization and depletion technologies to ensure that source depletion at DNAPL sites is implemented to the maximum extent practicable.

In particular, research is needed to address key knowledge gaps that still exist regarding the effectiveness and cost of these technologies for DNAPL source removal in a wide range of hydrogeologic settings. Research is needed on the following topics: (1) development, verification and comparison of alternative technologies for measuring mass flux and mass discharge from DNAPL source areas before and after source depletion; (2) improved predictive tools to estimate the benefits and adverse effects of partial source depletion for a range of DNAPL treatment technologies and DNAPL distribution and geologic scenarios; (3) continued field testing of DNAPL source depletion technologies incorporating more than one technology (e.g., thermal, *in situ* flushing or *in situ* chemical oxidation combined with biodegradation); (4) guidance on the conditions in which source depletion is not likely to be an effective strategy and containment must be relied upon; (5) assessment of the long-term water quality impacts of source depletion technologies; and (6) development of quantitative decision analysis tools that will permit an accounting of all potential costs, benefits, and adverse impacts of partial DNAPL source depletion. A major challenge is to identify the degree of characterization and post-remediation monitoring needed for effective application of each of the *in situ* source depletion technologies.

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