

Technical/Regulatory Guidance

Integrated DNAPL Site Strategy



November 2011

Prepared by The Interstate Technology & Regulatory Council Integrated DNAPL Site Strategy Team

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IDSS-1

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EXECUTIVE SUMMARY

Sites contaminated by chlorinated solvents present a daunting environmental challenge. Chlorinated solvents are prevalent and persistent groundwater contaminants, found at tens of thousands of sites worldwide. They also are among the most difficult groundwater contaminants to remediate, especially at sites with dense, nonaqueous-phase liquid (DNAPL) still present in the source zone. Restoring sites contaminated by chlorinated solvents to typical regulatory criteria (low parts-per-billion concentrations) within a generation has proven exceptionally difficult, although there have been successes. Site managers must recognize that complete restoration of many of these sites will require prolonged treatment and involve several remediation technologies. To make as much progress as possible within a generation (approximately 20 years) requires a thorough understanding of the site, clear descriptions of achievable objectives, and use of more than one remedial technology. Making efficient progress requires an adaptive management strategy and may also require transitioning from one remedy to another as the optimum range of a technique is passed. Targeted monitoring should be used, and reevaluation should be done periodically. Managers must implement effective and adaptive treatments that integrate more than one remedy to address complex contamination scenarios.

The ITRC Integrated DNAPL Site Strategy (IDSS) Team intends this guidance document to assist site managers in developing an integrated DNAPL site management strategy containing five key features:

- a **conceptual site model** (CSM) based on reliable characterization methods and an understanding of the subsurface conditions that control contaminant transport, reactivity, and distribution
- **remedial objectives** and performance metrics that are clear, concise, and measureable
- **treatment technologies** applied in sequence or in parallel designed to optimize performance and take advantage of potential synergistic effects
- **monitoring strategies** based on interim and final cleanup objectives, the selected treatment technology and approach, and remedial performance goals
- **reevaluating the strategy** repeatedly and even modifying the approach when objectives are not being met or when alternative methods offer similar or better outcomes at lower cost

This document describes key concepts and recent developments in each of these areas to help managers develop successful integrated strategies for chlorinated-solvent sites. The following sections summarize these concepts.

This IDSS guidance is intended for regulators, remedial project managers, and remediation engineers responsible for sites contaminated by chlorinated solvents. Because the subject matter is complex, this guidance is targeted towards experienced users; however, novices to the field will benefit from a thorough review of the text and accompanying references. The user of this guidance should be, or become, familiar with and practiced in the latest evolution of site characterization challenges; realistic planning of site restoration; evolving treatment techniques; and evaluating, monitoring, and interpreting mass transport in the subsurface aqueous and vapor phases. While the primary focus of the document is chlorinated-solvent sites, other types of contaminated sites (e.g., petroleum, mixed contaminants, etc.) can use the same fundamental process described in this guidance.

Conceptual Site Models

The CSM is the initial tool in developing an IDSS. CSMs for chlorinated-solvent sites should reflect the importance of source architecture (i.e., three-dimensional distribution of the chlorinated solvents), subsurface heterogeneities, and constraints on dispersive processes.

The CSM is important for sites contaminated by chlorinated solvents where the contaminant mass is typically distributed across several geologic media and may exist in more than one physical phase in the subsurface. Movement of contaminant mass between the four phases (DNAPL, vapor, aqueous, sorbed) impacts overall contaminant transport at a site. The importance of both the separate phases and their distribution between more and less transmissive regions is illustrated in the 14-Compartment Model shown in Figure ES-1.

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

Figure ES-1. Mass transfer at a chlorinated-solvent site depicted by the 14-Compartment Model. *Source:* Sale and Newell 2011.

A CSM should integrate several features:

- the site geologic and hydrogeologic setting
- the physical and chemical properties of the contaminants
- geochemical conditions
- physical, chemical, and biological attenuation mechanisms (e.g., sorption-desorption, oxidation, microbial reductive dechlorination)
- the relevant transport processes within and between compartments

Also, the CSM should describe all media that are impacted by the contamination, including the unsaturated and saturated zones, and any geologically and anthropogenically controlled heterogeneities that may be present. The CSM should also address the aging of sources, as most sources have been in place for decades and aging causes important changes in contamination properties and phase distribution that can affect the selection and success of remedial actions.

The limited hydrodynamic dispersion that can occur within plumes and sources is often surprising. The lack of dispersion results in the frequently observed extreme spatial variability in concentrations and mass flux, for example along a plume transect. Two models have been advanced to deal with mass transfer limitations between zones of high- and low-permeability media:

- the dual-domain, multiporosity model, which acknowledges that most flow occurs through a small fraction of the total volume (through preferential flow regions) but that long-term cleanup often is dominated by contaminant release from less-conductive zones
- the streamtube model, with large numbers of streamtubes, each having different contaminant concentrations and flow velocities but with limited mixing between these streamtubes

In contrast to the lack of dispersion, diffusion (e.g., mass transfer) has become an important process to incorporate in the CSM. Diffusion into less-transmissive zones has been known for decades, but its importance to the goal of restoration and the subsequent back-diffusion of contaminants into the transmissive zones have become increasingly recognized. At many sites back-diffusion can sustain plumes long after source removal and result in very long time frames for complete restoration of chlorinated-solvent source zones and associated groundwater plumes.

Remedial Objectives

Setting realistic objectives is critical when developing an IDSS. Objectives may be absolute (objectives based on broad social values, such as protection of public health) or functional (steps or activities taken to achieve absolute objectives, such as supplying bottled water to affected residents). Functional objectives are established to demonstrate attainment of absolute objectives and have often been missing, difficult to measure, or unattainable. A key concept of this guidance is that functional objectives should be specific, measurable, attainable, relevant, and time-bound (SMART).

Selecting objectives that reflect SMART attributes makes subsequent decisions more valid and remedial approaches more successful. It is often necessary to develop SMART functional objectives for different locations, phases, and alternative end points of an overall site cleanup. Given the unique perspectives of different stakeholders and the practical and economic limitations that exist, defining the SMART functional objectives appropriate for a given site requires cooperation, consensus, and often some compromises. An example site is used in this document to illustrate the potential functional objectives that may apply at a given site and how SMART criteria can be effectively applied when developing the final objectives.

Typical time frames involved in remediating chlorinated-solvent sites may be long (decades to centuries), but functional objectives should have relatively short time frames—years to less than one generation—to encourage accountability for specific actions and to make it easier to measure progress toward the objectives. The consensus of the IDSS Team is that functional objectives that extend beyond ~20 years are generally inappropriate, even though the absolute objectives may well require management and even subsequent active remediation well beyond such durations (see Chapter 3).

Treatment Technologies

Many technologies have been developed for source and plume treatment, all with specific advantages and limitations. Selecting a treatment technology requires evaluating several factors, including technical site features (e.g., geology, hydrogeology, and contaminant levels), regulatory requirements, sustainability, and community stakeholder interests. Traditionally, treatment technologies are applied individually at a site, with the expectation that one technology can achieve all objectives. More comprehensive approaches have gained favor recently for chlorinated-solvent sites because complete restoration can be difficult. These comprehensive approaches involve integrating several technologies in time and space.

To assist in evaluating technologies, this guidance includes general summaries of most of the applicable remediation technologies, along with data from site performance studies. In most cases, performance is expressed as both the percent reduction in source zone concentration and the number of orders of magnitude reduction observed. This focus reflects the typical situation at chlorinated-solvent sites, where concentrations in and near a source zone may exceed the cleanup criteria by three to five orders of magnitude or more and complete cleanup with one technology is rarely achievable. The guidance also includes resources available for screening-level assessments of remediation technology performance. Finally, the guidance addresses the potential compatibilities and concerns when combining different technologies that are summarized in a technology-compatibility matrix.

Monitoring and Modeling

A monitoring approach that relates remedy performance to site-specific SMART functional objectives is a critical element of an integrated strategy. The monitoring approach must include a spatially and temporally sufficient and reliable data set of the remedy performance. An appropriate monitoring program should be dynamic and adjusted to accommodate new data and changing conditions as remediation progresses. Monitoring programs should be routinely reviewed and adjusted to ensure that data being collected continue to be useful. The monitoring program should be designed to assist in making decisions about transitioning between technologies or implementing contingency actions.

Three types of monitoring are needed: **compliance monitoring** used throughout the remediation lifetime to document the nature and extent of impacts and to ensure that potential exposure pathways are controlled, **process monitoring** to assess whether the system is functioning as intended, and **performance monitoring** to assess effectiveness of the remedial approach in meeting SMART functional objectives. Typically, multiple lines of evidence are monitored to evaluate remediation performance. An effective performance monitoring approach enables decision makers to assess the value of the existing remediation program, identify required alterations of the existing remedial approach, and evaluate the progress toward meeting the functional objectives. The metrics most useful for this type of monitoring may not be typical monitoring data. For example, mass discharge and flux data may be more valuable for deciding when to convert from one technology to another than would concentration data alone. Similarly, relatively high-resolution monitoring data collected along transects may be valuable in

determining where to target treatments and in measuring performance. Transect-based data can also form a robust basis for measuring contaminant flux.

In developing a monitoring program, modeling is often helpful. Models can be valuable tools for assessing monitoring data, and useful models have been developed to assist managers of chlorinated-solvent sites. This guidance summarizes the features of several of the most widely used analytical and numerical models and describes their advantages and limitations. Regardless of the type of model, sensitivity analyses should be used to assess the potential impact of parameter values on simulation results and to develop a range of possible outcomes.

Reevaluating Strategies

Given the technical difficulties and need for several phases of remediation, it is normally necessary to reevaluate the overall strategy and its components at intervals. Such reevaluations are valuable in efficiently managing complex problems. The reevaluation involves answering a series of questions: (1) whether functional objectives are being met or whether the progress is acceptable; (2) whether the objectives can be achieved with greater efficiency (e.g., shorter time frames, lower costs); and (3) if the objectives are not being achieved, whether the remedy can be optimized or combined with another technology.

The first question is generally addressed under scheduled (e.g., 5-year) comprehensive site reviews but may be addressed to evaluate one particular remedial action or functional objective (e.g., whether source treatment reduced contaminant mass discharge within the first 5 years of a 20-year plume remedy). Such reviews should identify any changes that have occurred, rate of progress, any new potential risks, and any opportunities for improvement (i.e., optimization).

The second question should be raised at intervals because of the long time frames involved, the dynamic nature of environmental regulations and remedial technologies, and the ever-increasing understanding of the impacts of remedial actions (including green and sustainable practices). Even when a site is progressing satisfactorily toward its objectives, there is value in periodically evaluating options for cost reductions, changes in resource use (e.g., property transfer), incorporation of new technologies, and enhancement of existing systems.

The third question involves cases where the objectives are not being met. It is important to start by revisiting the functional objectives and the CSM because there can be many inaccuracies in a CSM that impact technology performance and it is common that the original objectives may need revision given new information. Assuming the objectives and CSM are still appropriate, the next step is to revisit the basis for the original technology selection because the actual performance of a technology is very site-specific and the database of information on technology performance at different types of sites is constantly growing. An iterative approach to troubleshooting technology performance is often required, and typical approaches include analysis of data trends, evaluation of whether the remedial action has reached a point of diminishing returns or even no recognizable benefit, and assessment of best practices involving determinations of whether the original technology has been improved or whether other more suitable and effective technologies are available.

Summary

The difficulties in remediating many chlorinated-solvent sites often make an integrated strategy necessary. The concept of an integrated strategy is not new although it has often proven difficult to implement. Developing an integrated strategy emphasizes the usefulness of a CSM that is based on a sound understanding of contaminant fate and transport, clear and achievable remedial objectives, a systematic treatment approach of two or more treatment technologies, a well-designed performance monitoring system, a defined process and time period for reevaluating progress, and an adaptive treatment approach. This IDSS does not suggest ignoring the regulatory requirements for site restoration, but it may mean leaving some contamination to be managed by longer-term treatment while using aggressive treatment technologies to reduce the site's risks. This IDSS guidance, including the examples presented as case studies, is intended to help site managers develop more efficient and effective integrated site management strategies through a collaborative process.

Integrated strategies should reflect our current understanding of chlorinated solvents in the subsurface where dispersion is often very limited and diffusion into and back from lower-permeability zones can be very important. An IDSS should define a series of SMART functional objectives and use treatment technologies where and when they are most appropriate to achieve those objectives. Functional objectives should be achievable within 20 years at most, even though site management and liabilities may continue for much longer.

When an IDSS in implemented, dynamic monitoring plans should be developed to measure progress towards achieving functional objectives and to determine when to transition to another more cost-effective technology. The monitoring plans should consider nontraditional metrics such as mass discharge and nontraditional approaches such as high-resolution transect monitoring. Any integrated strategy should be flexible, be adaptive, and identify contingency actions if results do not meet the expectations regarding performance. The strategy should also include deliberate reevaluations of the CSM and subsequence changes in the remedial objectives and remedial approach.

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INTEGRATED DNAPL SITE STRATEGY

1. INTRODUCTION

Sites contaminated by chlorinated solvents present a daunting environmental challenge. Chlorinated solvents are prevalent and persistent groundwater contaminants and are present at tens of thousands of contaminated sites worldwide. They are also among the most difficult groundwater contaminants to remediate, especially at sites with dense, nonaqueous-phase liquid (DNAPL) in the source zone. Restoring sites contaminated by chlorinated solvents to typical regulatory criteria (low parts-per-billion concentrations) within a generation (~20 years) has proven difficult. Complete restoration of such sites may require prolonged treatment and involve several remediation technologies. An integrated and strategic approach to chlorinated solvent– contaminated sites will support significant progress within a generation. Such an approach is built on a thorough understanding of the site and clear descriptions of achievable objectives. The resulting adaptive management strategy may also require transitioning from one remedy to another as the optimum range of a technique is passed. Targeted monitoring should be used and progress toward objectives periodically reevaluated.

This is not to say that complete restoration to such standards is impossible. To the contrary, there are examples where restoration to maximum contaminant levels (MCLs) or similar numeric standards has been achieved at chlorinated-solvent sites. However, most of these sites do not have significant DNAPL source zones that would allow removal by excavation. In fact, during preparation of this document, not a single example of a chlorinated-solvent site closure was identified where closure was based on achievement of MCLs throughout the entire site (including the DNAPL source zone) and without excavation.

For those chlorinated-solvent sites that have received regulatory closure, it was generally not based on complete restoration throughout the entire site. For example, the U.S. Environmental Protection Agency (USEPA) reports, "Sites profiled illustrate that addressing DNAPL source zones can lead to regulatory closure and, as is the case in six sites, unrestricted use" (USEPA 2009a). USEPA further reports, "Although this paper does not attempt to resolve this issue (e.g., benefits of source removal), it does provide information that illustrates instances where source reduction has contributed to achieving cleanup goals (maximum contaminant levels...)."

Compounding the challenge is the uncertainty associated with the benefits of partial source removal and the general lack of interim regulatory metrics or objectives to help define and incentivize partial source cleanup success. For example, some studies suggest that anything less than 80%–90% DNAPL source removal will result in only modest dissolved-phase contaminant concentration reductions in the downgradient plume (Falta, Basu, and Rao 2005; Sale and McWhorter 2001). Chapman and Parker (2005) suggest that even with complete DNAPL removal, contaminant diffusion into low-permeability zones can be a continuing source leading to dissolved-phase contaminant concentration reductions of only 1–3 orders of magnitude (OoMs). At the same time, 5 or more OoMs reduction may be needed to fully restore the site (Figure 1-1). USEPA (2009a) has concluded that "…the benefits of DNAPL source removal, especially partial source removal, are still being debated."



* Based on several multiple-site remediation performance studies.

Figure 1-1. Well-implemented in situ remediation projects are likely to reduce source zone groundwater concentrations by about one to possibly two orders of magnitude (90%–99% reduction) from pretreatment levels. *Source:* Sale et al. 2008.

As a result, an environment management strategy for DNAPL and chlorinated solventcontaminated sites should be developed on reliable data, be achievable, and be performance measureable. It must consider the limitation and uncertainty in our ability to fully characterize the subsurface and distribution of DNAPL and the removal, recovery, or treatment limitations of available remediation technologies. We can't ask for, promise, or certainly achieve miracles; therefore, realistic expectations and time frames should be discussed and agreed to by the project managers, responsible parties, and regulators. To completely remediate a site, this process may occur several times to iteratively establish achievable and measurable remedial objectives.

1.1 Purpose of this Guidance

The purpose of this guidance is to provide users with a process for developing an integrated DNAPL site strategy (IDSS) for managing the challenges of remediating a chlorinated solvent–contaminated site. Because of site similarities, this strategy can apply to any chlorinated solvent–contaminated site regardless of the presence of DNAPL. This guidance summarizes the latest

thinking in five key areas, based on experience and lessons learned, to help all parties involved maximize the chances for successful outcomes related to chlorinated site management and cleanup:

- a **conceptual site model** (CSM) based on reliable characterization methods and an understanding of the subsurface conditions that control contaminant transport, reactivity, and distribution
- **remedial objectives** and performance metrics that are clear, concise, and measureable
- **treatment technologies** applied in sequence or in parallel designed to optimize performance and take advantage of potential synergistic effects
- **monitoring strategies** based on interim and final cleanup objectives, the selected treatment technology and approach, and remedial performance goals
- **reevaluating the strategy** repeatedly and even modifying the approach when objectives are not being met or when alternative methods offer similar or better outcomes at lower cost

This IDSS guidance is intended for regulators, remedial project managers, and remediation engineers responsible for remediating chlorinated solvent–contaminated sites. Because the subject matter is complex, this guidance is targeted towards experienced users; however, novices to the field will benefit from a thorough review of the text and accompanying references. The user of this guidance should be familiar with, and practiced on, the latest evolution of site characterization challenges; realistic planning of site restoration; evolving treatment techniques; and evaluating, monitoring, and interpreting mass transport in the subsurface aqueous and vapor phases. While this guidance addresses chlorinated solvent–contaminated sites, other types of sites (e.g., petroleum hydrocarbons or other mixed contaminants, etc.) can be addressed using the same site strategy.

1.2 The Need for an Integrated Strategy for Chlorinated-Solvent Sites

Since the enactment of federal and state environmental laws in the late 1970s and early 1980s (e.g., the Comprehensive Environmental Resource, Conservation, and Liability Act [CERCLA] and the Resource Conservation and Recovery Act [RCRA]), numerous chlorinated-solvent release sites have been assessed, and remediation begun, typically focused on groundwater restoration. However, by the mid-1990s, monitoring data had revealed that many remedies and operational decisions were based on an incomplete CSM and a misunderstanding of the performance of remedial technologies in a heterogeneous environment contaminated with chlorinated solvents. As a result, many attempts at source zone cleanup have removed contaminant mass and reduced mass discharge but have not achieved their desired end points. For instance, USEPA (1999) reported that fewer than 10% of pump-and-treat (P&T) sites had attained closure but 80% had attained containment. Though remediation technologies have improved over time, in many cases achieving regulatory closure remains difficult and costly, and sometimes impractical, particularly when the goal is to restore groundwater to drinking water quality standards throughout the source zone and plume in, for example, less than 30 years.

1.3 Involving Indian Tribe and Public Stakeholders

Given the financial, technical, and regulatory complexities inherent in the remediation process; uncertainties in the application of various technologies; and the poor history to date in DNAPL

source zone remediation, it is highly recommended that effective communication be established with the stakeholders. In the context of this document, "stakeholders" consist of Indian tribes and public stakeholders, including citizens, community groups, advocacy organizations, and local officials. It is important to note that affected stakeholders are not necessarily limited to those in the immediate, local area around the site. For example, those who live downstream of a site may be affected even if they are not in the immediate vicinity. In the identification of affected tribes, it is necessary to consider that tribes may have treaties or other pacts with the federal government that grant them fishing, hunting, or access rights in places that are not necessarily near their present-day reservations. Furthermore, individual states and the Indian community recognize Indian tribes that are not necessarily recognized by the federal government.

Stakeholders generally show great interest in the contamination problem, remediation process, and effects that these have on human health and the environment. When planning remediation projects, the stakeholders should be fully informed of cleanup activities and potential consequences. A community relations plan should be prepared, and interested stakeholders should be involved, in the planning process even if it is from the emergency planning component. Many factors must be considered when determining the restoration project path, including the projected need for continuing surveillance and maintenance, institutional controls, engineered controls, local planning concerns, tribal government requirements, state regulators, and various stakeholders. In all cases, the process must have the goal of minimizing exposures to workers and the public, maximizing protection of the environment, and satisfying the concerns of the various stakeholders.

1.4 Is an IDSS a Site Closure Strategy?

This document is intended to promote the development of integrated strategies to improve cleanup and management of chlorinated-solvent sites and to maximize the chances for successful outcomes; however, this is not a site closure strategy. Not all chlorinated-solvent sites are alike; there is a range, from the relatively simple to extremely complex, depending on the size and depth of the source zone, presence or absence of DNAPL, hydrogeologic complexities, and age of the release.

On the technical side it has proven difficult to target and sufficiently treat the DNAPL within source zones in a realistic and predictable time frame. To achieve MCLs in DNAPL source zones, models, calibrated to remedial performance results, often predict cleanup time frames on the order of decades to centuries. But such predictions are highly uncertain, and our ability to measure meaningful progress toward such distant end goals is questionable. Furthermore, objectives that incorporate time frames of more than 20 years do not encourage accountability by the decision makers or take advantage of technology improvement, improved scientific understanding, and potential changes in the conditions of the site. In the end, objectives that require such long time frames can lose their relevance.

Consequently, attaining meaningful interim objectives that lead toward achieving closure standards, or alternative end points, may define success for many sites. For example, "success" could be defined in terms of achieving numeric cleanup standards everywhere throughout the source and plume, or it could be defined in terms of other interim or alternative objectives, such as the following:

- containing the source zone while achieving numeric cleanup standards in the downgradient plume
- transitioning to a passive remedy, such as monitored natural attenuation (MNA)
- achieving specific mass removal and/or mass discharge targets
- controlling human health or ecological exposures

IDSSs developed using this guidance provides a coherent strategy to improve the success of achieving site-specific objectives while optimizing remedial effectiveness, efficiency, and cost. An IDSS is not a silver bullet to achieve complete cleanup at any or all chlorinated-solvent sites. Rather, an IDSS can maximize the chances for successful outcomes through improvement of the CSM, development of SMART (specific, measurable, attainable, relevant, and time-bound—see Chapter 3) functional objectives, deployment of optimal treatment technologies and planned transitions, effective monitoring strategies, and strategic reevaluation.

1.5 When to Develop a Chlorinated Solvent–Contaminated Site Strategy

A strategy to reach a goal is certainly a good idea, and strategies are usually developed for most chlorinated-solvent sites. However, the core questions to ask when evaluating the performance of a chlorinated solvent–contaminated site strategy are as follows:

- How well is the current strategy working?
- If it is falling short in some regard, what else should be done?
- What technological improvements have become available that would work more efficiently?
- How can the CSM be improved?

An IDSS for a chlorinated solvent–contaminated site can be developed or updated at any point in the remedial process. Ideally, the strategy is created before any remediation has occurred and before much money has been spent. On the other hand, sites where remediation is already occurring (most common) can benefit from the development and/or update of the overall strategy.

1.6 Structure of the Document

Figure 1-2 both illustrates the process flow of IDSS development and represents the organization of this guidance. Each chapter uses small version of this flow diagram to help users track their progress in developing an IDSS. The five key areas of an IDSS, listed in Section 1.1, are represented in Chapters 2–6. Case studies (Appendix A) are used to highlight specific elements of each chapter. Even though no single case study can illustrate the use of an IDSS, Appendix B describes the development of an IDSS using an example based on real site characteristics. Chapter 6 describes a process to reevaluate a remedy and correct an underperforming remedy, transition to a different remedy, or improve the existing remedy. Not surprisingly, Chapter 6 is the point where most chlorinated-solvent site management teams begin, reflecting the fact that most teams have probably been managing their sites for a significant period and are now asking, "How are the current measures working, and what else might be done?"



Figure 1-2. Integrated DNAPL remediation decision making.

2. CONCEPTUAL FRAMEWORK FOR THE BEHAVIOR OF DNAPLS AND CHLORINATED-SOLVENT PLUMES IN THE SUBSURFACE

This chapter provides an overview of the subsurface behavior of DNAPLs and chlorinated-solvent plumes. Understanding these behaviors is crucial to а comprehensive understanding of any specific chlorinated-solvent site and therefore key to developing an accurate CSM, a critical component of the IDSS. A CSM describes the relationship of the source to the dissolved plume and other phases (e.g., vapor), including the site-specific transport mechanisms and receptor exposure pathways. The CSM is a framework for expressing site-specific knowledge that is then used in site management decisions. USEPA (in press) states that the life cycle of a CSM "mirrors the common progression of the environmental cleanup process where available information is used, or new information acquired, to support a change in focus for a project. The focus of a CSM may shift from characterization towards remedial technology evaluation and selection, and later, remedy optimization."



Parallel to USEPA's life-cycle CSM statement,

Figure 1-2 includes the CSM as the initial phase in development of an IDSS. CSM development begins when planning the site characterization, and the model is continually revised as additional information is generated during site remediation. The CSM is used during development of site remediation objectives and is updated during and after evaluation, selection, implementation, and monitoring of remediation technologies. Thus, the CSM supports development and evaluation of remediation objectives and treatment alternatives.

Section 2.1 of this chapter discusses the elements of a CSM and its role in developing and implementing an IDSS. Section 2.2 describes the key processes involved in the movement, reaction, and attenuation of chlorinated solvents in the subsurface. Section 2.3 highlights the importance of geologic conditions that control subsurface transport and, thus, many remediation processes. Section 2.4 describes issues pertaining to plume dynamics over time, including plume growth/attenuation and subsurface responses to treatment across different media and contaminant phases.

Chlorinated-Solvent Source Zones

A common perspective is that source restoration focuses strictly on subsurface media that held or hold remnant nonaqueous liquid-phase mass—the "DNAPL source zone." Groundwater restoration scientists and engineers now recognize the following:

- There is no bright line of demarcation between the "source zone" and the "diffuse plume."
- Over time a large fraction of the chlorinated-solvent mass may migrate into the aquifer matrix, and this mass can still act as a reservoir of contaminants that sustains the plume.
- Many of the challenges of groundwater restoration at DNAPL sites arise as much from natural aquifer structure as from the characteristics of DNAPLs themselves.

Section 2.5 presents a tool, the 14-Compartment Model (Sale and Newell 2011), which provides a framework to track chlorinated-solvent mass in the subsurface and how its distribution within subsurface compartments relates to treatment goals, remediation alternative selection and design, and site monitoring. Section 2.6 presents an example of a chlorinated-solvent site and development of its CSM. (This site is used in subsequent chapters to illustrate other elements of an IDSS and decision making.)

This overview of the behavior of DNAPLs and chlorinated-solvent plumes in the subsurface highlights key issues in development of a CSM. In-depth treatment of all technical issues is not provided. Instead, the goal of this chapter is to identify the key technical issues to be considered when developing a CSM. Additional literature citations are provided where appropriate, including previous ITRC documents that address pertinent technical and regulatory considerations.

2.1 The Conceptual Site Model

A CSM is a comprehensive description of a site used to support characterization or remediation planning and implementation. While there are a number of definitions for a CSM, it generally describes the relationship of the source to the plume and other affected media and includes contaminant fate and transport mechanisms and potential exposure pathways (ITRC 2004b). The CSM can also incorporate other societal or regulatory considerations, such as land use, community plans, and risk management scenarios. The CSM is a powerful, useful tool for project

Conceptual Site Model

A CSM is a framework for sitespecific knowledge that can guide site management decisions. The CSM describes the site, including the relationship of the source to the dissolved plume and other impacted phases (e.g., vapor) and site-specific transport mechanisms and receptor exposure pathways.

decision makers. It is often presented using a variety of media, including text, maps, cross sections, two- or three-dimensional graphics, physical or mathematical models, tables, charts, and other visual representations. The CSM is a working hypothesis and should be tested and revised as new site data are gathered.

The CSM is especially important for chlorinated solvent–contaminated sites because at any given time chlorinated solvents are typically distributed across multiple geologic media and occur in more than one chemical phase in the site subsurface. Movement of contaminant mass between these phase-media "compartments" impacts overall contaminant transport at a site (Pankow and Cherry 1996, Reynolds and Kueper 2001) and the response of one compartment to treatment of another (Chapman and Parker 2005; Parker, Chapman, and Guilbeault 2008; Kavanaugh et al. 2003; Stroo et al. 2003; Falta, Rao, and Basu 2005). These interrelationships also impact the efficacy of remediation efforts and ultimately determine the success of a remediation approach. For example, if source treatment is used to reduce plume concentrations, then the relationships between a source and its plume, and the expected response of both to treatment, must be understood. Similarly, if vapor impacts to indoor air are to be eliminated via groundwater plume remediation, then the relationship between groundwater, soil gas, and indoor air volatile organic compound (VOC) concentrations, and the response in these media and phases to groundwater treatment, must be understood as part of the CSM.

In summary, the CSM must be based on the site geologic and hydrogeologic setting as well as the physical and chemical properties of the contaminants, the site geochemical conditions, and the relevant transport and attenuation mechanisms within and between phase-media compartments. The CSM must describe all media that are impacted, including the vadose and saturated zones, and geologically and anthropogenically controlled heterogeneities, as well as multiple chemical phases (i.e., DNAPL, vapor, dissolved, or sorbed) that may be present.

2.2 Key Subsurface Transport and Reaction Processes

This section is an overview of the key transport and reaction processes that occur during and after subsurface releases of chlorinated solvents. Pankow and Cherry (1996) present a more detailed review of chlorinated-solvent transport and occurrence.

Chlorinated solvents are usually released in liquid phase (DNAPL) though in some cases an aqueous solution containing dissolved VOCs may be released. Once in the subsurface, the chlorinated solvents can exist in four phases: DNAPL, aqueous, vapor, or adsorbed. The adsorbed phase is normally associated with organic carbon, although other forces can contribute to soil adsorption.

Mass transfer among the four chemical phases (Figure 2-1) distributes the chlorinated-solvent mass

in accordance with equilibrium constants, although each rate can be modified by multiple chemical and physical processes (Mackay 1991). Diffusion limitations on interphase mass transfer are particularly important because these can significantly slow mass transfer of chlorinated solvents from the DNAPL phase into the aqueous, vapor, and sorbed phases. Diffusion also controls the rate of mass attenuation in the later life-cycle stages of a release. Diffusion occurs at the soil pore scale over distances of a few millimeters in a single geologic media, as well as at larger scales between different domains defined by geologic heterogeneities. The effects of geologic heterogeneity are discussed in greater detail below.



Figure 2-1. Chemical phases involved in the subsurface mass distribution of chlorinated solvents.

In the vadose zone the vapor phase is significant in terms of mass storage and transport, while in the saturated zone the vapor phase is essentially absent under most conditions (Figures 2-2 and 2-3). Capillary forces interacting with the aquifer matrix control the movement and distribution of the DNAPL in the subsurface. Most soils, sediments, and bedrock matrices are typically water-wet in the saturated zone, which means that water occupies the smallest pore spaces and preferentially coats the subsurface matrix. DNAPL is generally nonwetting with respect to the aqueous phase, which means that DNAPL has to overcome the capillary retention of water in the pore spaces to migrate through the saturated zone. The direction of migration is controlled by the mass of the DNAPL column and the size of the pore spaces, with preferential flow in the larger pore spaces that have lower capillary forces for the DNAPL to overcome. These migration pathways can be very tortuous due to heterogeneities in the subsurface. Though denser than

water, DNAPLs may migrate horizontally or in other directions than expected due to the size and distribution of preferential pathways.



Figure 2-2. Pore-scale distribution of chemical phases of chlorinated solvents.

Reactions that degrade or transform chlorinated solvents are very important to the subsurface fate and transport of chlorinated solvents. Naturally occurring reactions include microbial degradation and chemical degradation reactions. The most common attenuation reaction for chlorinated ethene is reductive dechlorination (ITRC 2008b), where under the proper reducing conditions, tetrachloroethene (or perchloroethene [PCE]) is reduced to trichloroethene (TCE), *cis*-1,2-dichloroethene (cDCE), vinyl chloride (VC), and ethene. The reader should be keenly aware that the degradation of a particular compound can significantly slow down as the reaction proceeds or the biological reductive dechlorination sequence can be interrupted by oxidative biological processes or abiotic degradation mechanisms.

The above processes interact to control the fate and transport of chlorinated solvents following a subsurface release. The following assumes the initial release is in the form of a DNAPL. Initially, DNAPL displaces air and/or water from the pore spaces. Then, as gravity moves DNAPL downward, it can leave a trail of residual blobs or ganglia of DNAPL, held in place by capillary forces.

When released in sufficient volumes, DNAPL can also form continuous bodies referred to as "pools." As shown in Figure 2-4, DNAPL pools may occur on top of low-permeability layers. Where DNAPL is present as a mixture of compounds, individual constituents of the DNAPL dissolve into water, sorb to solids, and partition into soil gas at different rates based on their physical and chemical properties and the percentage of each compound in the DNAPL. This fact reinforces the point that managing chlorinated solvents is not just about managing DNAPL. It is also about managing DNAPL constituents dissolved in water, sorbed to solids, and volatilized into soil gas.

2.3 The Importance of Geologic Conditions

Further insight into the key subsurface transport processes affecting a chlorinatedsolvent release is gained by recognizing the importance of the heterogeneous geologic conditions, as shown in Figure 2-4. There two main consequences are of heterogeneity: the location and distribution of DNAPL (DNAPL architecture) and diffusion of dissolved solvents from relatively transmissive zones to lowpermeability zones.

DNAPLs preferentially move through zones with the greatest permeability and transmissivity. The highest permeability and most transmissive portions of the subsurface matrix may be very small and





take up only a fraction of the aquifer matrix. In low-permeability portions of the subsurface, DNAPL can be largely precluded from entering these areas by capillary forces. An important exception occurs where secondary features such as fractures, root casts, or animal borings are present in low-permeability layers. In the end, subsurface DNAPL occurrence is often conceptualized as sparsely distributed fingers of DNAPL ganglia and pools. Intervals where DNAPL is present are surrounded by intervals that are largely free of DNAPL. The sparse distribution of DNAPL partially explains why it is difficult to locate during characterization work.

Another consequence of preferential pathways is that high concentrations of dissolved contaminants in the transmissive zones drive contaminants into low-permeability zones via diffusion. Within low-permeability saturated zones, contaminants are stored as an aqueous phase in water and as a sorbed phase on or in solids. The process of contaminants moving into low-permeability layers via diffusion is referred to as "matrix diffusion." The significance of contaminants in low-permeability portions of the matrix is that they diffuse back (back-diffuse) into the higher transmissive zones once concentrations in the latter decrease (see Text Box 2-1). Thus, back-diffusion can sustain dissolved plumes in transmissive zones long after the DNAPL

source is gone (e.g., Chapman and Parker 2005; AFCEE 2007; Payne, Quinnan, and Potter 2008; Sale et al. 2008). However, the degree to which contaminants diffuse into lowpermeability layers and are later released varies with the volume and concentration of the original source, distance from the source, time from release, and relative permeability of the subsurface strata. Figures 2-5 and 2-6 illustrate the process by which contaminants are stored and released from low-permeability zones.

Text Box 2-1. Air Force Plant 44, Diffusive Storage (see Appendix A)

A new CSM indicated that even though soil vapor extraction (SVE) had effectively removed TCE from the vadose zone, chlorinated-solvent contamination was still discharging to the downgradient aquifer due to diffuse storage in fine-grained materials in the capillary fringe and in the upper part of the aquifer material. SVE did not effectively remove this material.



2.3.1 Geologic Heterogeneity

Groundwater contamination first captured national attention in the 1960s and 1970s. At that time, environmental restoration practitioners did not realize the importance of aquifer matrix heterogeneity as a primary factor controlling contaminant migration. Even today, CSMs are often based on an assumption of the plume spreading within a uniform homogeneous aquifer.

Many traditional hydrogeologic tools average subsurface properties over large scales (hundreds or thousands of yards/meters or miles/kilometers). Aquifer pumping tests are typically analyzed with solutions, such as the Theis equation, that assume homogeneous, isotropic conditions and result in volume-averaged hydraulic properties. While this information is relevant for evaluating well productivity, the limitations of neglecting heterogeneity when evaluating solute transport were recognized by Theis (1967) himself: "I consider it certain that we need a new conceptual model, containing the known heterogeneities of natural aquifers, to explain the phenomenon of transport in groundwater." The frequent neglect of geologic heterogeneity persists to this day, as more recently stated by de Marsily et al. (2005): "Hydrogeology has been too much inclined toward hydraulics and solving of the flow equations, and not enough toward geology and understanding/describing the rock structure, facies, and properties in a geologically realistic manner, thus proposing 'exact' solutions, but to poorly posed problems."

Unfortunately, traditional hydrogeologic tools do not accurately represent or account for the importance of geologic heterogeneity within a single plume or even on a single contaminated site. The oversimplification of subsurface geologic conditions leads to the elliptical contaminant isoconcentration lines often drawn on plan view maps or in hydrogeologic cross sections. In reality, plumes migrate primarily in the most transmissive portions of an aquifer, which are surrounded by lower-permeability media that store and release contaminants via diffusion. This more refined and realistic conceptual model of contaminant transport has been supported by natural gradient tracer studies (Mackay et al. 1986; LeBlanc et al. 1991; Rivett, Feenstra, and Cherry 2001; Payne, Quinnan, and Potter 2008) and in recent years by high-resolution characterization of groundwater plumes resulting from chlorinated-solvent source zones

(Guilbeault, Parker, and Cherry 2005; Einarson and Mackay 2001), which has led to several observations:

- Order of magnitude changes in groundwater contaminant concentrations occur over short distances (often a meter or less from a source) transverse to flow.
- Chlorinated-solvent concentrations in the cores of plumes, at large distances downgradient of source zones, are often similar to concentrations in source zones.
- Transmission of the vast majority of plume mass can occur through a very small portion of the subsurface.

These observations have led to the realization that hydrodynamic dispersion of contaminants is likely a weak process in the absence of geologic heterogeneity and that geologic heterogeneity is the dominant control over contaminant plume spreading.

At scales of 1–100 m, subsurface heterogeneities and anisotropies lead to complex groundwater flow and contaminant mass transport patterns, especially for chlorinated solvents where DNAPL transport, interphase mass transfer, and diffusion are each strongly controlled by subsurface heterogeneity and together control the development of groundwater plumes. Field tracer studies (Mercado and Halvey 1966; Mackay et al. 1986; LeBlanc et al. 1991; Hall, Luttrell, and Cronin 1991; Stephens et al. 1998, Payne, Quinnan, and Potter 2008) have shown that a relatively small portion of most aquifers having the greatest permeability form preferential pathways where the highest groundwater and contaminant flows occur and where the actual transport velocities are much greater than aquifer-wide estimates made using traditional, large-scale averaging methods that assume homogeneous conditions. This understanding of subsurface transport processes suggests that the common approach of averaging out heterogeneities and representing the subsurface as homogeneous inadequately represents the subsurface and makes it more difficult to predict contaminant migration and restore groundwater quality to acceptable levels.

Many common hydrogeologic tools can underestimate or incorrectly represent the effects of geologic heterogeneity. Analytical contaminant transport models that assume homogenous conditions essentially average flow and transport processes throughout the plume and, therefore, understate maximum transport velocities in heterogeneous media. Further, numerical models are often discretized with a low level of geologic detail due to a lack of high-resolution site characterization data. This limitation affects plume flow and transport estimates in the same manner as seen with analytical models. Analytical or numerical models that underrepresent heterogeneity must instead explain documented plume spreading using unrealistic dispersivity terms. Overall, preferential flow and transport in the heterogeneous conductive zone are often underestimated (underrepresented), and lateral plume spreading is often overestimated.

Substantial literature exists that describes porous media flow processes and modeling in the presence of multiscale heterogeneities. Upscaling techniques and other approaches to more accurately predict flow and transport in multiscale heterogeneous media also exist (Frippiat and Holeyman 2008), but detailed characterization data to enable their use are lacking at many contaminated sites. Even where mathematical upscaling techniques are used to represent effects of multiscale heterogeneities in flow models, this approach may not pinpoint the high-flow zones at a site that may transmit most of the contaminant flux. Fully penetrating monitoring wells often





provide incomplete an representation of site conditions (Figure 2-7). Wells with long screened intervals average results over the screen interval and likely do not detect high-concentration and high-mass flux zones that are limited in vertical extent. As a result, fully penetrating monitoring wells mav underrepresent maximum contaminant concentrations by an order of magnitude or more.

Where warranted by project is beneficial goals. it to characterize aquifer structure at a resolution sufficient to properly subsurface account for heterogeneity and to physically heterogeneities identify kev dominating contaminant transport. Such an approach produces an understanding of site hydrogeology sufficiently

detailed to support development of a realistic CSM and a successful IDSS. Depth-discrete VOC sampling and/or relatively high-density grids or transects are the most obvious of high-resolution characterization data. Ideally, high-resolution characterization of subsurface geologic conditions and hydraulic properties should be conducted. The higher-resolution characterization approach also improves understanding of contaminant mass flux (Guilbeault, Parker, and Cherry 2005; ITRC 2010b).

2.3.2 Aquifer Structure—A Multiporosity System

The structure of preferential-flow regions at heterogeneous sites and their interaction with lessconductive zones often controls contaminant distribution and transport. If the subsurface is actually heterogeneous but is treated as if it were homogeneous, then a very small effective porosity must be used to explain the actual transport velocities. However, since porosity is a property of a representative elementary volume of the porous media, using it as a lumped parameter (averaged over a large volume of heterogeneous media) ultimately misrepresents the actual subsurface transport process (Zheng and Bennett 1995).

Most if not all subsurface environments can be thought of as having mobile and immobile (i.e., markedly less mobile) porosity domains, which impact or even control contaminant transport. The concepts of dual-porosity and dual-permeability domains have been used to conceptualize and model mobile and immobile systems in fractured and highly heterogeneous subsurface

environments (Warren and Root 1963; van Genuchten 1985; Berkowitz, Bear, and Braester 1988). Dual-porosity and dual-permeability flow models essentially overlay the mobile and immobile media within a single element of the subsurface. Dual-porosity models divide the total porosity within each element between a mobile porosity that transmits flow and an immobile porosity that is relatively stagnant. In a dual-permeability model, both media within each element can transmit flow with different assigned hydraulic conductivity values. Both dual-porosity and dual-permeability models simulate diffusive transport between the mobile and immobile media within each element. A number of mathematical vadose zone and groundwater flow and transport models incorporate dual-domain (i.e., dual-porosity or dual-permeability) representations, including MT3DMS (Zheng and Wang 1999), MODFLOW-2005 CFP (Shoemaker et al. 2008), MODFLOW SURFACT (HydroGeoLogic 1998), Hydrus (Simunek, Sejna, and van Genuchten 1999), and PHREEQC (Parkhurst and Appelo 1999). Dual-domain flow and transport models still represent a simplification of real-world conditions and therefore have inherent limitations. Nonetheless, where specific conditions and objectives warrant, they may represent an improvement over traditional, single-domain modeling approaches.

An alternative to the dual-domain approach is the streamtube approach, where flow characteristics in individual streamtubes are varied to represent flow in heterogeneous media. Streamtube flow models have been used to conceptualize heterogeneous flow and to simulate experimental data, primarily to evaluate petroleum production (Lenormand 1995, Lenormand and Wang 1995, Emanuel and Milliken 1997). Streamtube flow models have not been incorporated into groundwater flow simulators as have dual-domain models except at a research level (Finkel, Liedl, and Teutsch 1998).

In summary, the use of single-media or single-porosity concepts to characterize heterogeneous systems mandates the use of a very small effective porosity which, in turn, underrepresents the profound influence of heterogeneity on transport. The value of effective porosity is also often overestimated using specific yield or other parameters that are not representative of heterogeneous transport conditions. This practice can lead to a dramatic underestimation of actual transport velocities in the mobile portions of the aquifer. On this basis, Payne, Quinnan, and Potter (2008) suggested that the terms "mobile porosity" and "immobile porosity" are more appropriate than the terms "total porosity" and "effective porosity" to describe heterogeneous subsurface systems The dual-porosity concept may represent an improvement in the representation of highly heterogeneous media although the absolutely explicit prediction of contaminant transport and plume evolution is still a highly elusive goal. The dual-porosity approach, an increase in the use of higher-resolution site characterization methods, and the incorporation of more small-scale heterogeneities in transport models are all more explicitly accurate approaches to representation of chlorinated-solvent plumes. Depending on project goals, these more advanced methods may be justified to support development of a CSM and an IDSS.

2.3.3 Bedrock Systems

Groundwater flow and contaminant transport in bedrock systems are typically dominated by secondary fracture porosity with matrix diffusion of contaminants into and out of primary porosity significantly affecting contaminant flow and distribution in the aquifer (Parker, Gillham, and Cherry 1994). The dual-domain, multiporosity model used to describe flow in

unconsolidated materials as discussed above can also describe contaminant transport and groundwater flow in bedrock. The porosity available for movement of fluids in bedrock is commonly subdivided into three classes (Sowers 1981):

- Primary porosity—the openings between individual grains of rock, which can range from negligible (metamorphic rock) to high (sandstone). The rate of matrix diffusion is a function of primary porosity.
- Genetic porosity—the openings associated with specific depositional materials or environments, examples of which include lava tubes, tufa tubes, hollow-grained volcanic ash, and diatomaceous limestone.
- Secondary porosity—the openings or discontinuities in a rock matrix caused by breakage, fracture, or dissolution, which are further subdivided by origin as faults, joints, or karst channels.

Secondary porosity is frequently the dominant pathway for rapid fluid flow in fractured rock, while primary and genetic porosity play an important role in storage or retention of groundwater contamination. The fractures typically occupy a very small fraction of the aquifer matrix volume, but the hydraulic conductivity of the fracture zone is normally quite high. As a result, fractured bedrock can form low-water-volume, high-transport-velocity aquifers. Payne, Quinnan, and Potter (2008), for example, report natural gradient tracer studies in fractured sandstone where the tracer migrated more than 12 m per day. When slug and pumping tests in this aquifer were analyzed using calculation tools designed for homogeneous, isotropic porous media, the estimated average groundwater velocity for the formation was less than 3% of the observed transport velocity. Observations such as these call attention to the importance of aquifer structure in groundwater flow and solute transport.

The occurrence and nature of porosity and groundwater flow paths are exceedingly complex, and there is much research under way on methods of characterization, modeling, and prediction. The subject resists quick summation on all but the most superficial level. Readers are encouraged to explore further information available on the Internet, such as "Multidisciplinary Characterization of Contaminant Transport in Fractured Rock, Mirror Lake, New Hampshire" at http://toxics.usgs.gov/sites/mirror_page.html (USGS n.d.).

The multiple porosity and highly heterogeneous nature of fractured rocks requires an extension of current contaminant flow theory and field methods. It is particularly important that theoretical developments be applicable on a scale commensurate with field measurements.

2.4 Chlorinated-Solvent Source and Plume Dynamics

This section describes how chlorinated-solvent plumes form and evolve, as well as how they attenuate and respond to treatment.

2.4.1 Maturation of Subsurface Chlorinated-Solvent Releases

It is essential to remember that chlorinated-solvent releases continue to evolve (Figure 2-8). Immediately after a chlorinated-solvent release, the source area is dominated by DNAPL. With time DNAPL dissolves, and plumes develop while contaminants accumulate in low-permeability zones. Ultimately, little or no DNAPL remains, and plumes are sustained by the release of contaminants from low-permeability zones via diffusion (back-diffusion) (Chapman and Parker 2005). Although recoverable DNAPL may be found within some source zones, it is notoriously difficult to find DNAPL. At some sites (see late stage in Figure 2-8), it simply may not be there any longer, even though the source zone still contributes contaminant mass to the downgradient plume. Key factors controlling the rate at which chlorinatedsolvent releases evolve include the amount of chlorinated solvent released, effective solubility of the DNAPL constituents, rate of groundwater flow, and the architecture of the relative permeabilities.

Critically, at some sites impacted by chlorinated solvents, DNAPL may never have been present, for example, a site where wastewater with high aqueous concentrations of chlorinated solvents was stored in an unlined pond.

2.4.2 Source and Plume Response to Treatment

This section discusses several key processes involved in the subsurface response to treatment, including the impact of source treatment on plume mass flux and concentration and the response of chlorinated-solvent concentrations in soil vapor and indoor air to groundwater plume treatment. These topics illustrate the importance of a CSM that realistically represents the interactions between chlorinated-solvent mass in different subsurface compartments.



Figure 2-8. Multiple stages in the evolution of a chlorinated-solvent release site. *Source*: Sale et al. 2008.

The relationship between DNAPL mass removal and reductions in mass flux from sources zones is a subject of ongoing research. See *Use and Measurement of Mass Flux and Mass Discharge* (ITRC 2010b) for a detailed discussion of mass flux and mass discharge measurements and applications.

While it might be assumed that there is a one-to-one relationship between DNAPL mass removal and mass flux reduction, the DNAPL architecture and heterogeneity at a particular site influence this relationship. Published studies have found that in some cases (e.g., when DNAPL is isolated from the high-permeability flow paths) mass flux reductions greater than the degree of DNAPL source removal have been reported. In instances where the subsurface is more homogeneous, mass flux was reduced less than the extent of DNAPL source removal (Brusseau et al. 2008, DiFilippo and Brusseau 2008).

Research has shown that geologic DNAPL. heterogeneity and distribution/architecture are kev factors that control the relationship between source mass depletion and reduction of plume flux (Falta, Rao, and Basu 2005; Jawitz et al. 2005). Basu, Fure, and Jawitz (2008) compared the results of complex numerical simulations using the UTCHEM simulator to simplified analytical models of source depletion (e.g., Falta, Rao, and Basu 2005 and others) in terms of their ability to accurately predict the relationships between source mass depletion and plume flux reduction. They showed that the simplified analytical models provided а reasonably accurate estimate of the source-plume relationship, as indicated in Figure 2-9, which illustrates the following key concepts:



Figure 2-9. Comparison of modeled relationships between source mass depletion reduction and predicted plume flux reduction obtained using UTCHEM-generated simulations (symbols) and simplified analytical solutions (solid lines) for a range of geologic heterogeneity conditions represented by the log of hydraulic conductivity variance. Source: Basu, Fure, and Jawitz 2008.

- The simplified analytical solutions (lines in Figure 2-9) closely approximate the UTCHEM numerical simulations (symbols in Figure 2-9).
- The source mass flux reduction and the plume flux reduction do not follow a 1:1 linear relationship for most site conditions.
- For heterogeneous sites (large variance in Figure 2-9), a small fraction of source mass reduction results in a relatively greater plume flux reduction, reflecting that the plume flux is controlled predominately by the higher-permeability zones, which are where source treatment preferentially occurs.
- For homogeneous sites (small variance in Figure 2-9), a large fraction of source mass reduction results in a relatively smaller plume flux reduction, reflecting that in the absence of geologic heterogeneity, a partial reduction in DNAPL mass does not significantly decrease the DNAPL dissolution rate into flowing groundwater.

The primary factor affecting the different curves in Figure 2-9 is heterogeneity, expressed as the variance in the natural log (ln) of the hydraulic conductivity (K) in the various geologic media at the site. Other factors that control the source-plume relationship following partial source treatment include the specific DNAPL geometry with respect to heterogeneity and other parameters such as the DNAPL ganglia-to-pool ratio and other geometric factors. Numerical simulators such as the UTCHEM code explicitly account for these factors, while the simplified analytical models use a lumped fitting parameter (e.g., "gamma" in Falta, Basu, and Rao 2005) to account for these factors. Basu, Fure, and Jawitz (2008) developed a regression relationship between the variance in ln K and the model-fitting parameter gamma used by Falta, Basu, and Rao (2005), which can be used to estimate a value of gamma for a site.

In summary, understanding source and plume response to remediation is a key question at many sites. Site managers ask questions such as, "Will source remediation alone meet site goals?", "What will happen if no action is taken?", "Should I combine source and plume remediation?", and "What is a reasonable remediation objective?" One powerful but relatively simple tool that can be used to help with these questions is USEPA's REMChlor model (Falta, Rao, and Basu 2005; Falta et al. 2006). REMChlor combines a source zone model based on the gamma function above with an advection-dispersion model for chlorinated solvents. Two strengths of REMChlor are that is it can simulate how a source responds to remediation without the need for high-resolution source zone architecture data and that it can show, in a general way, how the plume will respond to partial source zone and/or plume remediation. Weaknesses are that, while it can simulate matrix diffusion effects in the source, and it has the theoretical disadvantages of the advection-dispersion approach (see Section 5.3.3 for a more detailed discussion). Overall however, both researchers and practitioners have found REMChlor to be a relatively simple but powerful groundwater model for evaluating remediation at chlorinated-solvent sites.

2.4.3 Vapor Intrusion

Management of potential risks associated with vapor intrusion is increasingly becoming a regulatory driver for site cleanups. The most basic instance of risk associated with vapor intrusion is derived from contaminated vadose zone soils, while in other instances volatilization of contaminants from groundwater is associated with vapor intrusion. Although this document is not largely focused on vadose zone impacts, their management plays an integral role in developing an integrated strategy for managing sites with DNAPLs. In some cases, regulatory agencies and responsible parties have negotiated (or are considering) site-specific groundwater cleanup criteria selected to be protective of indoor air in buildings above or near the groundwater plume.

Figure 2-10 shows an example from USEPA of a CSM cross section for potential subsurface vapor intrusion pathways (USEPA 2002, ITRC 2007c). The figure illustrates that the saturated groundwater zone represents only a portion of the overall mass of chlorinated solvents in the system and that the capillary fringe forms the actual boundary condition for soil vapor migration

into the vadose zone. The transient following processes in situ groundwater treatment that controls the attenuation of soil gas concentrations of organic vapors includes a combination of interphase mass transfer, desorption, diffusion, and advection. While the processes involved in soil gas organic vapor following attenuation in situ groundwater treatment have not been previously reported in the published literature, it is expected that some period of time will be required before the chlorinated-solvent mass in the vadose zone attenuates to a new chemical equilibrium with the decreased groundwater concentrations, especially if the vadose zone is highly heterogeneous and contains а reservoir of chlorinated-solvent mass in lower-permeability regions.



Figure 2-10. Conceptual model for subsurface vapor pathways. Source: USEPA 2002.

2.5 Introduction to the 14-Compartment Model

The 14-Compartment Model (Sale and Newell 2011) is used in this document to illustrate a number of key concepts. The following sections introduce the 14-Compartment Model and illustrate its application to assess the stages of plume maturity and to represent conditions at an example site. Subsequent chapters of this volume make use of the 14-Compartment Model to illustrate relevant concepts related to developing and implementing an IDSS.

2.5.1 The 14-Compartment Model

The 14-Compartment Model is a tool to aid in developing a simplified conceptualization of subsurface releases of chlorinated solvents. It is used to represent conditions in the saturated zone, and although the concepts could be applied to conceptualize contaminant impacts in the vadose zone, this step is not undertaken in this document. The 14-Compartment Model provides a holistic view of chlorinated-solvent phases within the saturated zone and their distribution in transmissive and low-permeability zones in source zones and plumes. The model also assists in the expected compartment response to treatment. Finally, the 14-Compartment Model can be used to assist in setting site remediation goals and to evaluate remediation alternatives and site monitoring data. It may not be necessary to numerically characterize all fluxes between compartments.
The 14-Compartment Model is not a numerical or analytical model—instead, it provides an organized framework to assess contaminant mass transfers between the source zone and plume and between relevant compartments within the source and plume regions. It provides a screening-level analysis of the benefits of potential remedial measures. The following are highlights of the model:

- The 14-Compartment Model was developed with a focus on mass transfers between compartments, not on static mass storage. Although the data used to assess mass transfers could also be used to approximate contaminant mass in storage, the model is focused on mass transfers to best support remedy selection and design.
- Contamination in each compartment is represented by a qualitative gauging of the chemical potential, which has been expressed as an "aqueous-phase-equivalent concentration." By using chemical potential (or its surrogate), we can see whether diffusive transfers are occurring and in which direction they are going.
- Mass transfers can be advective or diffusive. Transport in transmissive zones is primarily advective, while transport within lower-K zones (and between lower-K and transmissive zones) is dominated by diffusion.
- Advective transfers are irreversible; diffusive transfers are reversible, with the exception of diffusion-controlled dissolution of DNAPL.
- Transfers between low- and higher-K zones are predominantly diffusive.
- Diffusive transfers flow from compartments with higher chemical potential to compartments with lower chemical potential.
- As a source becomes exhausted and plume structure evolves, compartments that were net recipients of contaminants early in the source/plume development can become net sources of mass transfer late in the plume evolution process. The problem evolves from one of contaminants in transmissive zones to one of contaminants in lower-permeability zones through time.

Chlorinated solvents can occur in four phases in the source zone (DNAPL, aqueous, sorbed, and vapor) and three phases in the plumes (following NRC 2005, there is no DNAPL in plumes). Each of these phases can occur in subsurface zones that can be classified as "transmissive" (mobile) or "lower permeability" (immobile). Figure 2-11a provides a key to the locations of each of the 14 compartments at a hypothetical spill site. DNAPL has entered the subsurface, and there is DNAPL in the vadose zone as well as the aquifer. The aquifer comprises sand (transmissive) and clay (lower-permeability) zones. The source zone is defined as that portion of the site that has (or once had) direct contact with the DNAPL, and the plume is the portion of the site downgradient from the DNAPL zone that will receive contaminants via dissolved-phase advective transport.



Figure 2-11a. Key to compartment locations for the 14-Compartment Model.

Table 2-1a shows a 14-Compartment Model representation in blank tabular form. One way to use the 14-Compartment Model is to fill in such a table with qualitative estimates of the chemical potential in each compartment. Then, mass transfers between compartments can be anticipated as contaminants flow from zones of higher chemical potential to zones of lower chemical potential. The transfers may be advective or diffusive. Table 2-1b shows the transfers that are possible among the various compartments.

		ompai anche miou	ci ili biullis tubulu	1 Ioi mat		
Zone	Source	ce	Plume			
	Lower permeability	Transmissive	Transmissive	Lower permeability		
Vapor						
DNAPL						
Aqueous						
Sorbed						

 Table 2-1a. The 14-Compartment Model in blank tabular format

 Table 2-1b. The 14-Compartment Model with common contaminant fluxes between compartments (Solid arrows are reversible fluxes; dashed arrows are irreversible fluxes.)

		Plume						
Phase/Zone	Lov Permea	v Ibility	Transmissive		Transmissive		Low Permeability	
Vapor	† 1	-	•	† • • • • • • • • • • • • • • • • • • •		-	→ ,	t
DNAPL	•		•		NA		N	A
Aqueous	÷	•	*				→ ↑	Ļ
Sorbed	ţ				ţ		Ŧ	

Table 2-2 fills in a table to represent the site situation shown in Figure 2-11a, just after the DNAPL spill occurred. At this stage, the chemical potential in the DNAPL phase is high, and there has been little mass transfer into other compartments. At this early stage of spill site maturation, the mass transfers are primarily from the DNAPL into other compartments.

	0,		5		
7	So	ource	Plume		
Zone	Lower K	Transmissive	Transmissive	Lower K	
Vapor	LOW	MODERATE	LOW	LOW	
DNAPL	LOW	HIGH			
Aqueous	LOW	MODERATE	MODERATE	LOW	
Sorbed	LOW	MODERATE	LOW	LOW	

Table 2-2. 14-Compartment Model filled in for the early-stage spill site represented in Figure 2-11a (At this stage, contamination moves from the DNAPL into adjoining compartments.)

In transmissive zones aqueous- and/or vapor-phase chlorinated solvents are carried with the flow of water or soil gas. In contrast, low-permeability zones are largely stagnant from a flow perspective. Critically, low-permeability zones store and release contaminants via diffusion (Freeze and Cherry 1979; Sudicky 1986; Parker, Gillham, and Cherry 1994; Chapman and Parker 2005; Sale et al. 2008).

As an introductory illustration, Figure 2-11b shows the 14-Compartment Model analysis of P&T in a source zone. P&T is usually considered an inefficient approach for depleting contaminants in source zones. However, since the technology recovers aqueous-phase chlorinated solvents from the transmissive portion of the source zone, a benefit of source zone P&T is reduced loading of aqueous-phase contaminants to transmissive zones in the downgradient plume.



Figure 2-11b. Using the 14-Compartment Model to evaluate the potential value of pumping groundwater from a DNAPL source zone. Arrows show the diffusion of net mass transfers between compartments. Dashed arrows indicate diffusion-dominated transfers between compartments; solid arrows indicate advection-dominated mass transfers.

The following points provide an analysis of the mass transfers associated with groundwater extraction from a DNAPL source zone as depicted in Figure 2-11b:

- Pumping groundwater from the source will provide direct depletion of aqueous-phase contaminants in the transmissive portion of the source zone.
- If present, DNAPL will provide persistent release to the aqueous phase in the transmissive zone through dissolution.
- DNAPL may also be directly recoverable, especially during early-time pumping.
- Pumping groundwater from the source zone will provide direct depletion of aqueous-phase contamination from adjacent portions of the plume through advective mass transfer.

- Depletion of contamination in the transmissive zones results in the slow release of aqueous contaminants in lower-K zones, largely through diffusive mass transfer.
- Depletion of contamination in the transmissive zones also results in the slow release of sorbed-phase contaminants in lower-K zone, also through diffusive mass transfer. Note that the release of sorbed-phase contaminants can be a slow process.

Unfortunately, slow recovery of contaminants from adjacent compartments mandates long-term pumping.

2.5.2 Evaluating Overall Contaminant Distribution and Plume Maturity Using the 14-Compartment Model

Table 2-3 provides a 14-Compartment Model illustration of the early, middle, and late stage plumes described in Section 2.4.1.

Table 2-3. Illustration of the progression of a DNAPL-sourced plume through time that results from mass transfers between compartments using the 14-Compartment Model

(Groundwater flow [advection] carries contaminant from the source zone into the plume zone, and both diffusive and advective mass transfers can eventually distribute contaminants to all compartments. Over extended periods, contaminants can be diluted to lower concentrations, with

Zana	So	urce	Plume		
Zone	Lower K	Transmissive	Transmissive	Lower K	
Vapor	LOW	MODERATE	LOW	LOW	
DNAPL	LOW	HIGH			
Aqueous	LOW	MODERATE	MODERATE	LOW	
Sorbed	LOW	MODERATE	LOW	LOW	
7	So	urce	Plume		
Zone	Lower K	Transmissive	Transmissive	Lower K	
Vapor	MODERATE	MODERATE	MODERATE	MODERATE	
DNAPL	MODERATE	MODERATE			
Aqueous	MODERATE	MODERATE	MODERATE	MODERATE	
Sorbed	MODERATE	MODERATE	MODERATE	MODERATE	
7	So	urce	Plume		
Zone	Lower K	Transmissive	Transmissive	Lower K	
Vapor	LOW	LOW	LOW	LOW	
DNAPL	LOW	LOW			
Aqueous	MODERATE	LOW	LOW	MODERATE	
Sorbed	MODERATE	LOW	LOW	MODERATE	

stored mass in the lower-K zones acting as persistent sources of contamination.)

The transmissive zones of early stage plumes contain the highest VOC concentrations in their sources, particularity near the DNAPL phase. Over time the early-stage DNAPL phase, based on aqueous-phase equivalent concentration, is diminished by advection, biotic and abiotic degradation, and mass transfer into lower-permeability regions and other chemical phases within

the source as well as the plume. In a middle stage, the aqueous-phase equivalent concentrations across affected phases and zones are relatively equal. In late-stage plumes, contaminant concentrations have attenuated in the more permeable (transmissive) zones, and the larger remaining concentrations remain in the lower-permeability zones within both the source and the plume. These concepts are a useful part of site-specific CSM development because plume maturity has a large effect on the response to treatment of a source and plume and therefore the potential efficacy of possible remediation efforts.

2.6 Application of the 14-Compartment Model to an Example Site

The following example is based on an actual site. It is used repeatedly in each chapter to follow to illustrate the application of the concepts and approaches introduced in each chapter supporting the development of an IDSS.

2.6.1 Characteristics of the Site

The Washington Square Mall was constructed in 1978. One tenant, a dry cleaner, released unknown quantities of PCE into the soils and subsequently into the underlying aquifer over a 2-year period. Approximately 130 tons of DNAPL containing soil was excavated and disposed as a hazardous waste in 1990. The community and state government are concerned that the property has fallen into disuse and is becoming dilapidated, with a 20% occupancy rate in 1999. A local developer is interested in redeveloping the property for commercial/retail use (i.e., its historic intended use) and is evaluating the life-cycle costs for remediating the site.

The subsurface is composed of approximately 13 feet of clayey silt, overlying 6 feet of silty sand. Clayey silt below the silty sand zone extends at least another 10 feet below grade surface (bgs). Groundwater flows from the southwest to the northeast; depth to groundwater fluctuates 5–7 feet bgs. Residual PCE contamination has been measured in the soil at 4000 μ g/kg and in groundwater at 180 μ g/L near the point of release (the source area). There has been no remaining DNAPL confirmed/identified at the site; however, residual PCE continues to discharge into the underlying groundwater. PCE contamination has migrated approximately 200 feet downgradient of the point of release. There are no commercial buildings or residential homes downgradient of the site, and there are no potential adverse impacts to nearby drinking water wells.

2.6.2 14-Compartment Model Illustration

Figure 2-12 shows the CSM subsurface cross section integrated with the 14-Compartment Model. The 14-Compartment Model (Table 2-4) also depicts the order-of-magnitude distribution of contaminant concentrations. The concentration estimates in the aqueous and sorbed/residual cells in the source zone were developed from available water quality and soil gas data. The values in the transmissive zone of the plume were also developed from groundwater data. Concentrations in the other cells were derived as approximate expected values based on equilibrium partitioning between phases. Unfortunately, as is typical for many sites, no data were available from the low-permeability zones. When critical information is missing, efforts should be made to collect the information needed to make fully informed decisions. Thus, development of 14-Compartment Models can help decisions regarding collection of additional data. Overall, the Washington Square Mall resembles a middle-stage site (see Figure 2-8 and Sale and Newell

2011, Figure 11) where chlorinated solvent has apparently moved into the aqueous, vapor, and sorbed phases.



Figure 2-12. Cross-sectional representation of the contaminated Washington Mall site with the 14-Compartment Model mapping the phase distribution of the site.

Zone/	≩/ Sour			се			Plume						
phase	Low p	permeability	Trans	missive	Transmi	issive	Low permeability						
Vapor		2		3	1		1						
DNAPL	0		0 0										
Aqueous		1		1		1		1		2	2		1
Sorbed		3		3 3		2		1					
^a Concentrations in aqueous-phase equivalents (orders of magnitude):													
0 depicts >1 µg/L 1 depicts >10		µg/L	2 depicts >	•100 µg/L	3 depicts >1000 µg/L								

Table 2-4	. Washington	Square Mall PCE	contamination	in soil and	groundwater ^a

The establishment of achievable objectives is the next step in the process. The next chapter describes how to establish overarching objectives for the site and to reduce these to very specific, measureable, attainable, relevant, and time-bound (SMART) objectives.

3. **REMEDIATION OBJECTIVES**

At most sites, the objective of site restoration is to achieve MCLs in all impacted media, but this goal is often technically and/or economically impracticable within reasonable time frames. However, it is possible to develop remedies that address the most critical risks, foster partial cleanups, and address community concerns over time frames of a few years while continuing progress toward more complete restoration in the long term. Implementing such remedies requires careful development of reasonable functional objectives for actions that may not meet the concentration-based criteria established in regulations but that will reduce risks, enable development and use of sites, or allow transitions to relatively passive remedial options such as MNA.

This chapter describes a process for establishing absolute remedial objectives and developing functional remedial objectives to achieve those absolute objectives. Functional objectives are developed by considering the short- and long-term requirements of all



parties involved and should conform to SMART attributes (i.e., be specific, measurable, attainable, relevant, and time-bound) (Doran 1981).

3.1 Historical Perspective of Absolute and Functional Objectives

Environmental regulations and laws require that cleanup objectives for the remediation of multiple media at a given site be established and achieved. In CERCLA terminology, cleanup objectives are called remedial action objectives (RAOs) and can be either interim or final. In this document objectives are defined as either absolute or functional (NRC 2005; ITRC 2008b).

Absolute objectives are based on broad social values, such as protection of public health and the environment. Functional objectives are the steps or activities that are taken to achieve absolute objectives. Functional objectives are in fact RAOs (i.e., the objectives for a given set of actions), and they can be interim or final. But at many chlorinated-solvent sites, the functional objectives established for short-term actions do not represent final RAOs because the final RAOs often are not attainable within a reasonable time frame. An example of an interim functional objective might be to replace an impaired water supply with an alternative supply to prevent exposure within a month, while an example of a final functional objective might be to meet water quality objectives in the downgradient plume by 2020. Meeting all properly constructed and complete functional objectives should ensure that the absolute objectives are attained.

The problem is that remedial objectives for chlorinated-solvent site cleanups have often been illdefined, difficult to measure, or unattainable (NRC 2005, Kavanaugh et al. 2003), largely due to the difficulties achieving final RAOs based on MCLs or similarly low numeric standards in

DNAPL source zones, which include uncertain expectations for remediation effectiveness, technical and economic limitations, and measurability problems such as and accountability associated with long time frames (e.g., decades to centuries). Therefore, the challenge is to parse the problem (see Text Box 3-1) and develop SMART functional objectives for different locations or phases or develop functional objectives for an alternative end point of an overall site cleanup. SMART functional objectives add credibility to subsequent remedial design and implementation and establish a metric for monitoring remedial approaches that offer measurable and predictable progress over a credible period of time (≤ 20 years) while still meeting applicable regulatory requirements.

Site managers have used various approaches to set remediation objectives. A common approach has been to assess exposure pathways and pursue risk-based numerical cleanup standards throughout all applicable compartments impacted by the chlorinated-solvent release. Another approach is to pursue the most immediate risks/threats or develop objectives for specific locations within the plume or source zone. Other common approaches include developing objectives for when to transition to a more passive remedy or to pursue an alternative end point (Text Box 3-2). For example, if a determination is made that MCLs cannot be achieved in the DNAPL source zone in a measurable or relevant time frame, federal and state regulatory programs have allowed for other cleanup standards or objectives.

Text Box 3-1. Dry Clean USA, Well-Defined Objectives (see Appendix A)

At Dry Clean USA the primary project goal was to see whether treatment could reduce PCE concentrations to the Florida MCL of $3 \mu g/L$ throughout the aquifer and to $30 \mu g/kg$ for soil (based on leaching potential) so that closure (i.e., no further action) could be obtained from the state regulatory agency.

Additional soil objectives (set by the state's drycleaner program) included 30 μ g/kg TCE, 400 μ g/kg cDCE, 700 μ g/kg *trans*-DCE, and 7 μ g/kg VC.

Having such well-defined objectives allowed the appropriate technologies to be applied and a Site Rehabilitation Completion Order was issued within 8 years of the initial treatment.

Text Box 3-2. Well 12A, Tiered Remedial Action Objectives (see Appendix A)

Tier 1: Address residual sources, including principal threat wastes, minimize the risk to receptors due to contaminated surface soils, and achieve at least a 90% reduction in contaminant discharge from the high-concentration source area to the dissolved-phase contaminant plume.

Tier 2: Achieve the cleanup levels at interim performance monitoring points.

Tier 3: Determine whether cleanup levels can be achieved in a reasonable time frame throughout the entire contaminant plume by discontinuing the groundwater extraction and treatment system operation and implementing MNA of remaining contamination.

If the Tier 3 compliance is deemed infeasible, additional remedial alternatives will be evaluated, and/or a technical impracticability waiver may be sought for the noncompliant portions of the aquifer.

Examples of alternative objectives that can be used in specific instances include alternative numeric standards, under some programs referred to as "alternative concentration limits" (www.epa.gov/superfund/health/conmedia/gwdocs/acls.htm, Title 40 Code of Federal Regulations, Part 264.94 [40 CFR §264.94]) or "containment" of the plume (e.g., contained within a slurry

wall or upgradient of a permeable reactive barrier (PRB) or hydraulically with P&T). Under some programs, cleanup standards that differ from regulatory standards such as MCLs require exemptions or waivers, such as technical impracticability waivers under CERLCA (www.epa.gov/superfund/health/conmedia/gwdocs/tec_imp.htm).

At some sites it is possible to apply aggressive treatment of the source zone and dissolved phase and attain remedial objectives relatively quickly. At other sites, the time frame to attain the final functional objectives could be different for the DNAPL source zone than for the downgradient aqueous-phase plume. For example, a remedial approach could be designed to stabilize or treat the plume and control associated risks first, with reduction of mass discharge from the source zone as an interim objective. At Well 12A (see Text Box 3-2) compliance with RAOs was divided into three tiers to allow for implementation of the multicomponent remedy and decision making, such as when to transition from one treatment technology to another and when the site is transitioned to operation and maintenance (O&M). Reduction of mass discharge could be achieved using containment, treatment, or even partial removal of the source. This approach would allow use of a large portion of the aquifer, while the inherently difficult source remediation is addressed separately. Similarly, it may be necessary to immediately address offsite concerns, such as vapor intrusion, while plume remediation continues over a much longer time frame.

3.2 Developing SMART Objectives

The American Management Association (AMA), among others, recognizes the crucial role of developing good objectives prior to starting virtually any project. The AMA provides the acronym "SMART" to convey the attributes of good objectives listed earlier (Doran 1981). Functional objectives can be confirmed or adjusted to meet the SMART attributes by asking the diagnostic questions about each (see Text Box 3-3).

As pointed out earlier, the objectives set for cleanup of chlorinated-solvent sites have rarely been attainable or readily measurable. A handful of chlorinated-solvent sites have been remediated to the point of closure and unrestricted use (USEPA 2009a), but it is far more common to have residual contamination above MCL values even after aggressive treatment (NRC 2005) so that interim/alternative functional objectives are needed. Examples of such interim/alternative functional objectives concentrations and mass discharge to the point that passive site management can be used to contain and treat the residual contamination or to reduce risks to the point that development can proceed with appropriate exposure controls. The measurability of the objectives can be a concern, especially given the difficulties in measuring mass and concentrations in some compartments (e.g., lower-permeability zones) and the natural variations in groundwater data.

The planning time frame is an important consideration that deserves special discussion. A wide range of restoration time frames has been used for site cleanups, generally 30 to >100 years (based on team experience) or even longer. The time frame required to treat chlorinated solvents in groundwater to concentrations less than MCLs (typically an absolute objective) may be several decades to centuries, so shorter-term functional objectives are needed for meaningful and

measurable interim steps. The consensus of the IDSS Team is that detailed predictions beyond a human generation (~20 years) are generally inappropriate when setting functional objectives.

Do not confuse the maximum 20-year time frame used for setting SMART functional objectives (a planning time frame) with the time frame for completion of the absolute objectives (site restoration time frame).

There are four key reasons for restricting the time frames for SMART functional objectives at chlorinated-solvent sites:

- While absolute objectives may not be achieved for decades or more, functional objectives that extend beyond a generation (>20 years) do not encourage accountability by the decision makers involved.
- Natural variations in concentrations and aquifer conditions (e.g., groundwater elevations, geochemistry) make it difficult to measure progress towards objectives with longer time frames.
- The ability to make accurate predictions of performance beyond 20 years is questionable.
- Scientific and technical abilities are not static, and longer time frames do not account for these advances.

Text Box 3-3. Diagnostic Questions to Ensure Compliance with SMART Attributes

- **S Specific**—The objectives should specify what is to be achieved through a remedial action. They should be concrete, detailed, and well defined.
 - Diagnostic questions:
 - What exactly are we going to do?
 - o Is the objective well understood?
 - Will this objective lead to a desired result?
 - S does not mean "shifting"!
- M Measurable—Managers should be able to measure whether or not the objectives are being met. Numbers, quantities, or comparisons should be specified, and the uncertainty in key measurements should be understood.
 - Diagnostic questions:
 - $\circ~$ How will we know that the change has occurred?
 - Can these measurements be obtained?
 - *M* does not mean "magical"!
- A Attainable—Objectives should be realistic, given the proposed time frame, political climate, and/or the amount of money available.
 - Diagnostic questions:
 - Can we get this done in the proposed time frame?
 - Do we understand the limitations and constraints?
 - o Can we do this with the resources we have?
 - o Is this possible?
 - Has anyone else done this successfully?
 - A does not simply mean "ambitious"!
- **R Relevant**—The objective should have a value and represent a realistic expectation.
 - Diagnostic questions:
 - Does the outcome of the objective directly support achievement of the absolute objective?
 - Do we have the resources available to achieve this objective?
 - *R* does not mean "remarkable"!
- **T Time-bound**—The time allotted for achieving the objective should be clearly defined and short enough to ensure accountability.
 - Diagnostic questions:
 - When will this objective be completed?
 - Is someone still going to be accountable for meeting the time frame?
 - T does not mean "timeless"!

Although defining functional objectives with time frames of ≤ 20 years is encouraged, it is important to remember that the absolute objectives may well require management and even subsequent active remediation well beyond such durations. Further, some sites may show little

change over 20-year time frame, but some reassessment after 20 years seems prudent in light of likely technology improvements and possible changes in priorities. It is also important, however, to remember that sites will not be abandoned after this time, and responsible parties may well have to reserve funds for site management extending far beyond 20 years. Planning-level estimates of how long contamination and liability will remain under various remedial alternatives will still be required, and predictive models such as REMChlor (www.epa.gov/ada/csmos/models/remchlor.html) will still be useful for such long-term planning.

Selecting objectives that reflect SMART attributes makes subsequent decisions more valid and remedial approaches more successful. The following two sections help the user understand the range of input in the development of absolute and functional objectives for a site and how SMART functional objectives can be developed for the example site described in Section 2.6. Even though each stakeholder has an interest in the outcome and a unique perspective (e.g., the mayor of the city wants job creation, a developer wants unrestricted land use, and residents want future assurance of clean water), cooperation, consensus, and often some compromises are necessary to define the small number of SMART functional objectives for a given site.

These functional objectives, which are focused on potential exposure pathways and resource protection, then become the driving force for the remedial manager and define the steps necessary to design a remedial approach. The following section illustrates the range of potential perspectives and input into the development of possible objectives for chlorinated-solvent sites. Through discussions of these perspectives with all stakeholders, SMART functional objectives that eliminate, reduce, and control exposure and protect the environment can be better defined.

3.3 Examples of Possible Objectives for Chlorinated-Solvent Sites

The objectives in Table 3-1 represent examples of possible generic objectives for decision makers tasked with managing a chlorinated-solvent release (Sale and Newell 2011). It is unlikely and unwarranted that every objective be incorporated into one cleanup project as a SMART functional objective. However, applicable functional objectives from Table 3-1 could evolve into site-specific SMART functional objectives given a process of systematically evaluating each functional objective against the SMART attributes and diagnostic questions in Text Box 3-3.

The IDSS Team tested the process of making multiple objectives for a single site SMART and found that many of them become considerations rather than objectives. For example, "Longevity—Reduce the time period during which contaminants in source zones and plumes will provide persistent releases to the groundwater and or soil gas" and "Land use—Restore beneficial use of impacted lands" feed information into the risk objective "Prevent active adverse human exposure via groundwater or soil gas." This latter risk functional objective can then be used to drive remediation in a particular direction. This functional objective can then be tested against the SMART attributes and made to be specific, measureable, attainable, relevant, and time-bound.

Table 3-1. Examples of possible generic objectives for chlorinated-solvent sites(These could evolve into SMART functional objectives.)

Absolute Objectives
Protect human health and the environment.
Conserve natural resources.
Address adverse community impacts.
Minimize the burden of past practices on future generations.
Functional Objectives
Risks
• Prevent active adverse human exposure via groundwater or soil gas.
• Prevent active ecological exposure via groundwater or soil gas.
• Prevent adverse work-related exposures via soil, groundwater, and/or soil gas.
• Avoid actions that create new risks (do no harm).
Extent
• Prevent expansion of source zones and plumes.
• Reduce the extent of source zones and plumes.
Longevity
• Reduce the time period during which contaminants in source zones and plumes will
provide persistent releases to the groundwater and/or soil gas.
Regulatory
• Comply with local, state, and federal regulations.
Community
Address adverse impacts to communities.
Land use
Restore beneficial use of impacted lands.
Economic
• Select actions that have practical near-term capital costs and minimal life-cycle cost.
• Avoid undue interruptions to communities, government, and industry activities.
Remove or control adverse impacts to property values.
Sustainability
• Select measures that have a net positive environmental benefit.
• Restore the site to a state for which passive remedies will control residual impacts.
• Enhance the effectiveness of complementary technologies.
Resource Conservation
Limit future degradation of resources.
Restore impacted groundwater to beneficial use.
Protect sensitive biological receptors.

3.4 Examples of SMART Objectives for a Chlorinated Solvent–Contaminated Site

Using the example introduced in Section 2.6, the following section illustrates how difficult, yet important, it is to define the absolute objectives and associated SMART functional objectives for remediation of the example site. The drivers for site remediation are not only risk of exposure, but in this case, enhancement of property use or reuse and economic development as well.

Regardless, the performance metrics for remediation ultimately address risks to human health and the environment.

3.4.1 The Risk at the Example Site

Approximately 130 tons of DNAPL containing soil was excavated and disposed as a hazardous waste in 1990. Residual PCE contamination has been measured in the soil at 4000 μ g/kg and in groundwater at 180 μ g/L near the point of release (i.e., source area). No remaining DNAPL has been confirmed/identified at the site; however, residual PCE continues to discharge into the underlying groundwater. PCE contamination has migrated approximately 200 feet downgradient of the point of release (Figure 3-1). There are no commercial buildings or residential homes downgradient of the site and no potential adverse impacts to nearby drinking water wells.

A risk assessment showed the site did not pose an unacceptable risk to human health under the existing conditions. However, an assessment of the risks posed to potential occupants of a building that would be constructed at the site showed that the residual PCE in the soils would pose an unacceptable risk via vapor intrusion to indoor air. In addition, PCE concentrations in the groundwater would also support unacceptable vapor concentrations in indoor air. The assessments determined that residual concentrations of 40 μ g/kg PCE in soil and 8 μ g/L PCE in groundwater would reduce the risk via indoor air exposure to or below the de minimus level of a 1×10^{-6} incremental excess cancer risk. It was also determined that concentrations exceeding 45 μ g/kg PCE could leach to the groundwater at an unacceptable rate (see Section 2.6 to review details of the site characteristics and the 14-Compartment Model representation).

3.4.2 Drivers for Redevelopment at the Example Site

Institutional controls and monitoring might have been sufficient under existing conditions to protect against unacceptable exposure. However, the developer wanted to return the property to beneficial use in a relatively short time frame while avoiding any institutional controls. The redevelopment plan necessitated the evaluation of active remediation alternatives.

The community, health department, and regulatory agencies conditionally approved the redevelopment of the dry cleaning lot and the construction of a grocery store. The local developer hired a consultant to remediate the site within a year to regulatory requirements, which will protect future employees (i.e., absolute goal). To achieve this goal, the functional objectives were agreed upon by the regulators, community, health department, and developer. Time frames were determined by development needs.

3.5 Creating SMART Functional Objectives

To redevelop this property in consideration of the site characterization, the drivers for redevelopment with no land use restrictions applied after completion, and a defined time frame, the absolute objectives were determined to be as follows:

- Protect human health and the environment.
- Redevelop the mall area within its intended use.

Using the 14-Compartment Model to illustrate the general distribution of contaminants (Table 3-2), we recognize that we have the following (Figure 3-1):

- 1. source and plume vapor intrusion exposure pathway from the groundwater
- 2. source and plume vapor intrusion pathway from the underlying soils
- 3. PCE loading to the aquifer from the unsaturated zone
- 4. PCE and degradation products in the aquifer

Table 3-2. Washington Square Mall PCE contamination in soil and groundwater

Zone/	Source						Plume				
phase	Low permeability			Transmissive		Transmissive		Low permeability		ability	
Vapor		2			3		1			1	
DNAPL		0			0						
Aqueous		1 4	≜ '		2	<u> </u>	2	_ ≜ !			1
Sorbed		3	l		3		→ 2				
^a Concentrations in aqueous-phase equivalents (orders of magnitude):											
0 depicts >1 µg/L 1 depicts >10			µg/L	2 depicts >100 µg/L			3 depicts >1000 µg/L				



Figure 3-1. Cross-sectional representation illustrating potential exposure pathway according to 14-Compartment Model in Table 3-2.

Table 3-3 lists the functional objectives required to achieve the absolute objectives. Not unexpectedly, contingencies require institutional controls be established to control vapor intrusion if attainment of any of the first four objectives is delayed. All objectives must comply with all applicable federal, state, and local regulations during and following remediation.

Table 3-3. Functional objectives for Washington Square Mall conforming to the SMART attributes

Absolute Objective #1: Protect human health and the environment. Absolute Objective #2: Redevelop the mall area within its intended use.

- 1. Vapor intrusion pathway (soils): Reduce concentrations of volatile organics in the vadose zone that will allow "no further action" determination for unrestricted use, with no administrative or engineering controls required, for the soils within 6 months (vapor intrusion indoor air objective).
 - Specific—Yes: 40 µg/kg PCE highest measured residual concentration, an approximately 2 OoM reduction (1.0% residual) estimated from the high soil concentration of 4000 µg/kg
 - Measurable—Yes: achieving 40 µg/kg
 - Attainable—Yes: e.g., removal, SVE, in situ chemical oxidation (ISCO); institutional controls may be required if 40 µg/kg is not achieved
 - Relevant—Yes: intended reuse of the property
 - Time-bound—Yes: 6 months (development time frame)
- 2. Vapor intrusion pathway (groundwater): Reduce concentrations of volatile organics in the groundwater that will allow for "unrestricted use" of the property, with no administrative or engineered controls, within 18 months (protection against vapor intrusion).
 - Specific—Yes: approximately 2 OoM reduction from the highest groundwater concentrations
 - Measurable—Yes: achieving 8 µg/L PCE; values for other VOCs and other pathways will be determined if necessary
 - Attainable—Yes: ISCO and/or bioremediation
 - Relevant—Yes: intended use of the property
 - Time-bound—Yes:, 18 months (determined by development needs)
- **3.** PCE loading to the aquifer: Reduce concentrations of PCE in the vadose zone to eliminate/prevent further discharge of PCE into the underlying aquifer (prevent loading to the groundwater plume, stabilize and eliminate the groundwater plume).
 - Specific—Yes: approximate 2 OoM reduction is needed based on modeling
 - Measurable—Yes: achieving 40 µg/kg
 - Attainable—Yes: e.g., removal, SVE, ISCO; institutional controls may be required if 40 µg/kg is not achieved
 - Relevant—Yes: to meet developer's desire for unrestricted use of the property
 - Time-bound—Yes: 18 months (determined by development needs)
- 4. PCE and degradation products in the aquifer: Reduce concentrations of volatile organics in groundwater to background concentrations or drinking water quality in 2 years, allowing for no restrictions on the ability to use the water.
 - Specific—Yes: meet drinking water standards and/or background concentrations
 - Measurable—Yes: meet drinking water standards and/or background concentrations
 - Attainable—Yes: small extent, favorable hydrogeology, and coarse-grained soil allow ISCO and/or bioremediation or similar technology
 - Relevant—Yes: eliminates potential impact to existing or potential water supplies and the need for deed restriction that the developer does not want
 - Time-bound—Yes: 24 months

To confirm that we have SMART functional objectives, Table 3-3 documents that the functional objectives for the example site remediation conform to the SMART attributes. It contains a list of the functional objectives and SMART attributes with a corresponding rationale for "claiming" that the functional objective accommodates each SMART attribute given the level of detail known about the characteristics of the site and the maturity of the release (see Chapter 2). Each functional objective was collectively refined so that it meets all SMART attributes, based on the CSM. If an objective does not meet a SMART attribute, the result can, and likely will, be "less than optimal" or "unachievable." That result will likely require additional resources and more time and may never achieve the performance metric.

Table 3-3 describes each SMART attribute as it applies to each functional objective. Understanding the rationale used to claim the functional objectives meet all of the SMART attributes forms an important basis that can be referred to throughout the remedial process under any of the following circumstances:

- The chosen technologies do not perform as expected.
- An alternative treatment technology or system must be implemented.
- It is realized that the functional objective cannot be achieved.

In this case, the basis of the original functional objective can be reviewed and potentially used to understand what led to the wrong initial decision. If a problem should occur in the performance of the remediation, the basis of these claims can be revisited and used to assess the accuracy of the information that went into the claim. For example, Functional Objective 1 (Table 3-3) is as follows:

Reduce concentrations of volatile organics in the vadose zone that will allow "no further action" determination for unrestricted use, with no administrative or engineering controls required, for the soils within 6 months (vapor intrusion indoor air objective).

Functional Objective 1 is based on a good understanding of the mass transfer properties of the contaminants, the aquifer, and the vadose zone and the requirement that the property can be used for any purpose within 6 months. If at the end of 6 months unrestricted use is not possible, the data used to determine that such use was achievable in the given time frame and the technology to be used will come into question.

There is no assurance that each SMART objective can be achieved. There are financial restrictions on all projects, and the site professionals must make assumptions and inferences using the available data. Remediation of most chlorinated solvent–contaminated sites requires revisiting the CSM, the technologies and combinations of technologies implemented, and the functional objectives before the project is completed. Even after characterization compliance, process, and performance monitoring provide data that enhance what was previously known or suspected at a site. Use these data to refine the CSM, adjust or modify technologies, and reevaluate the likelihood of success.

In summary, it is a good idea to consider contaminant mass in all environmental compartments to develop SMART functional objectives at a chlorinated solvent–contaminated site. The

14-Compartment Model discussed in Section 2.5 and Table 2-2 is a tool that can help visualize compartments and set objectives. Compartmentalization offers a simplified representation of potential mass transport between phases and compartments of a chlorinated solvent– contaminated site. Subsequently, it helps define the applicable functional objectives for the phases or potential exposure pathways. Time frames for completing a functional objective should not exceed 20 years to remain relevant and maintain accountability, and progress toward objectives should be measureable within shorter time frames such as a few years. Following the flow diagram in Figure 1-2, Chapter 4 discusses the selection of an appropriate technology or combination of technologies (treatment trains) to achieve the functional objectives listed in Table 3-3.

3.6 ITRC Indian Tribe and Public Stakeholder Perspective of SMART Functional Objectives

The ITRC tribal and public stakeholder representatives note that applying SMART attributes to functional objectives increases the reliability of remedial objectives for a site. Even though the initial or interim functional objectives may not fully meet the absolute objectives without further management, iterative progress is more accurately promoted toward protection of human health and the environment. Specific diagnostic questions (Text Box 3-3) for applying SMART attributes give a succinct direction to the tribal and public stakeholder as to what should be asked and addressed when collectively developing remedial objectives for a site. In addition, setting time frames for SMART functional objectives of no more than 20 years establishes clearer individual responsibility for projections of progress than planning remediation and remedial objectives for 50, 100, or more years. Chlorinated solvent-contaminated sites are admittedly difficult, and the community and tribal stakeholders consider cleanup time frame and level of cleanup the most adverse impacts to the community. The functional objectives for the Washington Square case is a great example of the proper application of the SMART attributes that can be followed and used as a guide for the tribal and public stakeholders. Some flexibility is often necessary in the remediation process. This flexibility may be a cause for stakeholder concern since it might be seen as a loss of regulatory control over the remediation process. Using functional objectives with SMART attributes that are developed and accepted by all parties involved may alleviate some of the uncertainty in the approach of achieving long-term (absolute) objectives.

4. TREATMENT TECHNOLOGIES

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).

In this chapter, Section 4.1 presents general categories of remediation technologies applicable to chlorinatedsolvent sites. Section 4.2 discusses coupling technologies in time and space, including issues of compatibility. Section 4.3 describes how and when to consider transitioning from one or more technologies to new technologies. Section 4.4 presents methods to map



technologies and remediation performance for individual compartments using the 14-Compartment Model. Finally, Section 4.5 extends the example from Chapters 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 μ g/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 μ g/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.

Technology category	Example technologies	Example references					
Physical removal	Excavation	NAVFAC 2007					
	Multiphase extraction	USACE 1999a					
	Thermal conductivity/	Johnson, Tratnyek, and					
	electrical resistance heating	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.	Technology	categories
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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).

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 results.
- The performance studies are the only place where detailed before and after data have been made at multiple sites.
- Some of the performance studies are able to compare different technologies using a repeatable, consistent methodology.
- 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 conditions.

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:

- 99.9% 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:

 $OoM = -log[1 - (\% reduction \div 100)]$

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 posttreatment 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 \geq 2 OoMs (99%) for four sites. The mass flux reduction was estimated to be \leq 1 OoM at nine of the sites and \geq 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

compounds, saturated (ethane) and unsaturated (ethene) 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.

chlorinated aliphatics, while

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 soiladsorbed CVOCs caused contaminant concentrations to rebound after the oxidants were consumed.

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 (Olsen and Sale 2009). Data on EPA's CLU-IN website indicate nanoscale ZVI has been used for at least five projects (<u>http://cluin.org/download/remed/nano-site-list.pdf</u>). 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 chlorinatedsolvent 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%)groundwater plume treatment decision documents at Superfund sites from fiscal years 2005-2008 (USEPA n.d.), although not all of these contain sites DNAPL (DNAPL sites were not separately identified in the Superfund remedy data).

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 μ g/L and 24 μ g/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.

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 (Environetal Technologies, Inc.) indicates that ZVI PRBs have been constructed at 157 sites worldwide (www.eti.ca, accessed on April 9, 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 lowpermeability 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 changed.
- Remedial objectives changed as regulations and our understanding of risk control or management evolved.
- 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 cases.

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 chlorinatedsolvent 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.

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.

4.2.1 Spatial and 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 lowpermeability 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 step.
- 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 contaminants.

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 require 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.

	Followed by this	Physic	cal removal techr	ologies		Chemical/biolo	ogical technologies	6	Containmen	t technologies
Appl tech or in	technology or in downgradient area	Surfactant/ cosolvent flushing	Thermal technologies	Other extractive technologies	Chemical oxidation	Chemical reduction	Bioremediation	Monitored natural attenuation	Permeable reactive walls	Other containment technologies
_	Surfactant/ cosolvent flushing		Potentially comp	patible but not an a	anticipated coup	le (see Note 1)	Generally com Note	patible (see 1)	Potentially co an anticipate No	mpatible but not ed couple (see ote 1)
hysical remova technologies	Thermal technologies	Potentially compatible but not an anticipated couple (see Note 2)		Potentially con co	npatible but not a uple (see Note 2	atible but not an anticipated Generally compatible (see le (see Note 2) Note 1)		Potentially compatible but not an anticipated couple (see Note 2)		
<u>م</u>	Other extractive technologies	Potentially con an anticipate No	mpatible but not ed couple (see ote 3)			Generally com	patible (see Note 3)		Potentially compatible but not an anticipated couple (see Note 3)	
inologies	In situ chemical oxidation	Potentially c	compatible but not couple (see Note	an anticipated 4)		Potentially compatible but not an anticipated couple (see Note 4)	Generally compati consideration reagents (se	ble but requires of chemical ee Note 4)	Potentially compatible but not an anticipated couple (see Note 4)	Generally compatible (see Note 4)
cal tech	In situ chemical reduction	Potentially c	compatible but not couple (see Note	an anticipated 5)	Likely incompatible (see Note 5)	y tible Potentially Compati)
hemical/biologi	Engineered bioremediation	Potentially c	compatible but not couple (see Note	an anticipated 6)	Compatibility varies (see Note 6)	Potentially compatible but not an anticipated couple (see Note 6)		Generally compatible (see Note 6) Potentially compati an anticipated co Note 6)		mpatible but not ed couple (see ote 6)
Ū	Monitored natural attenuation		Potentially compatible but not an anticipated couple (see Note 7)						Potentially co an anticipate No	mpatible but not ed couple (see ote 7)
ontainment chnologies	Permeable reactive barriers	Potentially c	compatible but not couple (see Note a	an anticipated 8)	Likely incompatible (see Note 8)	Likely ncompatible see Note 8) Potentially compatible but not an anticipated couple (see Note 8)				
ç õ	Other containment technologies			Potentially comp	patible but not ar	n anticipated cou	uple (see Note 9)			

 Table 4-2. Technology compatibility matrix

Table 4-2 Notes

- 1. Enhanced extraction by surfactant/cosolvent flushing is generally compatible with anaerobic bioremediation and with NMA 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 necessary.
- 2. 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 necessary.
- 3. 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 technology.
- 4. 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 stabilization.
- 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 conditions. 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 ISCO.
- 7. MNA is potentially compatible with all other technologies, and in most chlorinated solvent remediation sites 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 site.
- 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 system.
- 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 changed.

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

site conditions evolving (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 transition developed. Possible triggers are as follows:

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.
- 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 chlorinatedsolvent 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 developed.
- Step 2 is to collect data. Site data are used to assess progress of the remedy towards the functional and absolute objectives.
- 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 remedy.
- Step 6 (for a negative answer to Step 4) is to evaluate whether the remedy can or should be optimized to improve performance.
- 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

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 μ g/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 μ g/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.

	Source				Plume							
Zone/	Low permeability			Transmissive		Transmissive			Low permeability			
phase	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.

	Source				Plume							
Zone/	Low permeability			Transmissive		Transmissive			Low permeability			
phase	Before	Technology	Aftor	Before	Technology	Aftor	After Defere	Technology	Aftor	Poforo	Technology	Aftor
		performance	Aller		performance	Aller Delore	performance	Allei	performance	Allei		
Vapor							1	2	0	1	1	0
DNAPL	1 Net en rieskie											
Aqueous			Not ap	plicable			2	3	0	1	1	0
Sorbed]					2	2	0	1	0	1	
	0 depicts >1 µg/L in aqueous- 1 depicts >10 µg/L in			2 depicts >100 µg/L in 3 depicts >1000 µg/L			L in					
	phase equivalent aqueous-phase equivalent				aqueous-phase equivalent			aqueou	is-phase equiv	alent		

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

5. DEVELOPING A MONITORING APPROACH

Development of an effective monitoring approach to evaluate progress towards achieving functional objectives is a critical element of an IDSS. As such, the monitoring approach must include a spatially and temporally sufficient and reliable data set measuring performance of the remedy. This chapter provides guidance and supporting material to assist the user in developing a monitoring approach that evaluates remedial performance toward SMART functional objectives. Useful related material includes USEPA 2005b and 2006.

An IDSS monitoring program links elements of the remedial approach (e.g., technology estimated performance) against the measured performance and to the IDSS SMART functional objectives using performance metrics and a dynamic monitoring approach. A dynamic monitoring approach has the ability to adjust as data are added and analyzed against the current CSM (see Chapter 2). While easily stated, developing measurement metrics within the context of a SMART functional objective is difficult (see Section 3.2).



This chapter provides guidance for development of a monitoring approach at a chlorinated solvent–contaminated site. Section 5.1 describes three types of monitoring, Section 5.2 describes various media to be monitored, and Section 5.3 offers insight into alignment of data collection with SMART functional objectives. Section 5.4 describes the various metrics used in site monitoring, Section 5.5 describes methods used to evaluate monitoring data, and Section 5.6 discusses optimization of a site monitoring approach. Finally, Section 5.7 again visits the Washington Square Mall example to illustrate how to align monitoring elements with SMART functional objectives.

Key questions to ask when developing a functional objective centered monitoring approach are as follows:

- What media should be monitored?
- What constituents should be monitored?
 - Beyond the COCs, what other parameters should be monitored to establish multiple lines of evidence to evaluate performance?
 - How many lines of evidence are needed for an assessment toward a functional objective?
- What metrics should be used?
- Where should monitoring points be located?

• When should monitoring occur?

5.1 Types of Monitoring

Three types of monitoring are typically used at chlorinated-solvent sites: compliance, process, and performance. The parameters monitored in compliance, process, and performance monitoring can vary (e.g., concentration at a monitoring well, the mass discharge leaving the source zone, or the pumping rate from a containment system). Decision makers design the monitoring system to provide useful information about the nature and extent of impacts, how well a remedial approach is operating, and how well a remedial approach is meeting planned expectations (i.e., SMART functional objectives). Each is described below:

- **Compliance monitoring** is used throughout the IDSS life cycle to document the nature and extent of impacts, as well as the status of exposure pathways. Investigation and characterization of chlorinated-solvent sites is the first step of systematic compliance monitoring. Compliance monitoring may also be included within process and performance monitoring, as discussed below, and therefore is an overall goal of an IDSS monitoring approach and the basis by which attainment of functional and absolute objectives is evaluated. Compliance decision making may require a higher level of certainty and be subject to nontechnical factors that lead to the use of different analytical protocols, monitoring locations, and/or monitoring frequencies than are required for process and performance monitoring.
- **Process monitoring** assesses whether a remediation system is meeting or approaching its functional objectives (ITRC 2008b). If not, process monitoring data are used to identify the need for adjustments and modifications to the remedial system(s) to improve performance (i.e., process optimization).
- **Performance monitoring** is used to assess the effectiveness of the remedial approach in meeting the SMART functional objectives (see Text Box 5-1). Typically, multiple lines of evidence or types of data are collected to measure the effects of remediation on the

concentrations or the mass discharge of COCs. the completeness of treatment, and the secondary impacts of remediation on groundwater quality. Effective performance monitoring approach enables decision makers to assess the of value the existing remediation program, required of the existing alterations remedial approach, and evaluation of the soundness (SMARTness) of the functional objectives.

Text Box 5-1. Fort Lewis East Gate Disposal Yard, Strategic Monitoring (see Appendix A)

The Fort Lewis East Gate Disposal Yard remedial action is a prime example case study showing how strategic monitoring resulted in more effective and efficient cleanup of chlorinated solvents. In 1998 an Explanation of Significant Difference was issued to allow further investigation into the nature and extent of the contaminants of concern (COCs) as well as to enhance the selected remedy. This understanding allowed innovative treatment strategies to be considered, such as the Triad approach for characterizing migration of COCs, as well as the use of ERH to remove the NAPL. Having this flexibility in place was instrumental in the practitioners' ability to make modifications during all phases of remedial action, from initial installation to relocating to the additional areas needing treatment, to ensure remedial process performance. Monitoring systems evolve to fill in data gaps, refine the CSM, and optimize the number of samples and analyses required to measure compliance, process, and performance. Each is not necessarily a distinct suite of subsurface monitoring methods and locations. Rather, samples can offer data for two or more of the monitoring types. For example, performance monitoring data at distance from a DNAPL source zone may also be used as exposure point compliance monitoring over the longer term or for permit compliance. This factor highlights the value of a complete CSM and an understanding of source-plume dynamics (see Chapter 2).

The following sections help the users query themselves to determine what, where, and when data should be collected and analyzed to evaluate elements of a remedial approach. The section also contains reference citations for previously developed step-by-step approaches to the development of the elements of a typical monitoring approach.

5.2 Media to Monitor

Functional objectives are evaluated by measuring contaminant or chemical relationships using concentration, for example, $\mu g/L$ (water), $\mu g/kg$ (solids), or mass moving through a vertical plane of the subsurface as mass flux ($g/d/m^2$) or mass discharge (g/d) (ITRC 2010b). Evaluation of chemical, physical, or biological processes in the subsurface that affect remedy performance and the distribution of COCs, depends on the media monitored. Media selection is influenced by functional objectives and potential exposure pathways. The sections below discuss media typically monitored at chlorinated-solvent sites.

5.2.1 Dense, Nonaqueous-Phase Liquid

DNAPL is the least commonly monitored media because DNAPL is difficult to locate and collect. DNAPL monitoring is limited due to the means in which DNAPL moves through the subsurface (Chapter 2). Screening for DNAPL during the site characterization phase can help determine whether the monitoring plan should include further DNAPL monitoring and/or screening. Since detecting DNAPL at a site is often difficult, high concentrations of dissolved-phase constituents (aqueous concentrations >1% of the DNAPLs solubility) are typically used to indicate DNAPL presence (Kueper and Davie 2009).

5.2.2 Aquifer Matrix Materials

Aquifer matrix material is sampled to determine the distribution and extent of chlorinated solvent constituents in the source zone. As the groundwater moves through the source zone, a plume of dissolved constituents moves away from the source zone. These dissolved constituents sorb to aquifer matrix material and diffuse away from zones with relatively higher concentrations into zones with lower concentrations. Sorption occurs within these less-transmissive zones where little to no groundwater flow occurs, effectively creating zones that later act as supplemental sources, which can sustain a groundwater plume after the more-transmissive zones are remediated. As a result, monitoring programs may include sampling the aquifer matrix material in various geologic strata.

Limitations to aquifer matrix monitoring include the following:

- high spatial and temporal variability in sampling results (Statistical methods and sampling procedures have been developed to address these issues, e.g., USEPA 2009b.)
- representativeness of samples due to small sample mass
- aquifer heterogeneity

These limitations can cause estimates of the mass of chlorinated solvents in the subsurface to be imprecise and unreliable. Nonetheless, the information obtained from samples of the aquifer matrix can be used to do the following:

- establish baseline aquifer matrix concentrations
- improve the understanding of the distribution of chlorinated solvents at a site
- monitor progress of contamination and remediation efforts
- modify the operational design of a remedy
- evaluate the completeness of a remedial action

5.2.3 Soil Gas

Soil gas sampling is useful at chlorinated-solvent sites to assess the potential for human exposure from vapor intrusion into indoor air and as a qualitative screening tool to rapidly detect DNAPL source areas in unsaturated soil (ITRC 2007c). Soil gas sampling data can delineate the areal extent of soil gas migration in and from the unsaturated zone. Soil gas sampling has also been used to evaluate conditions near the water table and the potential for groundwater to contribute chlorinated-solvent compounds to soil gas. Samples collected in a vertical profile can help delineate lateral or vertical migration of soil gas due to variations in the subsurface stratigraphy and vapor characteristics. To evaluate the potential for soil gas to cause a vapor intrusion (indoor air) exposure, sampling locations should be spaced to adequately represent soil gas concentrations near any structures, taking into consideration the location of contamination relative to the structures and atmospheric effects (ITRC 2007c). The actual number of soil gas sampling points necessary for a given site depends on site-specific conditions and is likely to change during the life cycle of a project. Location and installation of soil gas monitoring should consider the following:

- public concern over exposure through this pathway
- temporal variations due to the following:
 - o seasonal and short-term influences (e.g., barometric pressure, precipitation, or wind)
 - o remedial program impacts
- increased fundamental understanding of transport processes (e.g., retardation and partitioning)
- sample collection representativeness and uncertainty
- new sampling approaches

5.2.4 Groundwater

Groundwater monitoring programs collect data that intend to represent the concentration of contaminants, contaminant degradation products, water chemistry (pH, Eh, temperature), and other aqueous chemicals that may influence the behavior of chlorinated solvents dissolved in groundwater. Groundwater samplers are designed to obtain a representative water sample (e.g., low-flow sampler, Snap SamplerTM, HydraSleeveTM) or groundwater contaminant concentration value (e.g., GORE ModuleTM; regenerated-cellulose dialysis membrane sampler; rigid, porous polyethylene sampler; polyethylene diffusion bag sampler) from groundwater monitoring wells (ITRC 2004c, 2007b). However, groundwater sampling methodology can influence sample results, and care should be exercised when mixing results from various sample collection methods.

The design of a groundwater monitoring program should be based on the needs defined by the functional objectives, the CSM, and refinements to the CSM resulting from analysis of monitoring data over time. A groundwater monitoring program should achieve the following:

- monitor temporal or spatial changes in contaminant concentrations
- monitor changes in subsurface aquifer conditions such as geochemistry
- monitor progress toward regulatory compliance
- monitor contaminant concentration or mass in potential exposure routes
- assess mass balance (e.g., determine the baseline mass in the different compartments, or the media they represent, using groundwater concentration and soil mass values, mass reduction due to remedial actions, and mass discharge to groundwater (in conjunction with aquifer hydraulic properties)
- assess and demonstrate remedial efficiency (process monitoring)
- assess remedial effectiveness (performance monitoring)
- confirm completion of treatment and site closure

Groundwater monitoring programs should be periodically reviewed and optimized to ensure that the data being collected continue to be useful and relevant in achievement of site-specific functional objectives. As remediation progresses and subsurface conditions change, the groundwater monitoring program should evolve.

5.2.5 Surface Water

Depending on the site, surface water may be part of the monitoring strategy. The discussion in this guidance is not focused on sites where a groundwater plume is discharging to surface water. While surface-water analytes may be similar to groundwater analytes—concentration of contaminants, contaminant degradation products, and water chemistry (pH, Eh, temperature)— surface water metrics should also include parameters such as near-shore and off-shore hydraulic head, sediment characteristics, and direct seepage measurements. Guidance on surface-water monitoring discussing monitoring techniques such as Trident Probes and UltraSeep, as well as standard water-column collection, can be found in ITRC 2011b.

Surface water monitoring program should consider the following:

- groundwater-to-surface water discharge locations
- monitoring depth
- how the data will be used

5.3 Aligning Data to SMART Functional Objectives

Site decision makers establish a two- or three-dimensional monitoring system that evaluates the progress of the remedial approach using the metrics defined to measure performance within the time frame outlined in the SMART functional objective (see Table 3-3 for examples of metrics and time frames). Table 5-1 illustrates potential monitoring approaches for examples of functional objectives. Citations are provided to guide the user to more detailed information for specific, contaminant phases, media, and target contaminants.

5.4 Metrics

To assess overarching functional objectives such as exposure, extent, fate, and transport of chlorinated solvent in a source zone or plume, as well as progress of remedial actions, SMART attributes need to be assigned to the functional objectives. Through that process, a specific, measurable quantity or metric must be selected for each media to be monitored. Typically, metrics are selected in either concentration or mass units. However, mass flux/discharge is emerging as a new and useful metric at chlorinated-solvent sites. A monitoring strategy can include a combination of concentration, mass flux, and mass discharge metrics.

5.4.1 Concentration

Contaminant concentration is the traditional means for assessing soil, groundwater, and soil gas and is typically the metric for assessing the site's remedial progress and compliance. Compliance values are typically a concentration-based metric implying protectiveness. A groundwater analytical value represents only an average contaminant concentration in water over the sample interval controlling the flow of water into or past the sampling device during the time of the sample collection. This is an important consideration given the emphasis concentration data have on the decision-making process. A rigorous assessment of sampling methodologies, the methods' influence on the sample results, and their relationship to the metric measuring conformance with the functional objectives should be carefully considered in the monitoring approach. Bias in sampling methods (e.g., the effect of pumping rate on the groundwater sample, seasonable influence, etc.) should be recognized and given due consideration.

Functional objectives	Media to monitor	Information resources				
	Risks					
Prevent active adverse	Groundwater in drinking water wells should be monitored for priority pollutants (e.g.,	ITRC 2000b, 2003, 2008b,				
human exposure via soil	VOCs) or COCs to ensure that MCLs are not exceeded.	2010b				
gas and/or groundwater	Potential for vapor intrusion via contaminated soil gas should be monitored for VOCs.	ITRC 2007c, 2007d; USEPA				
	Selection of measurement location (subslab, soil gas, indoor air) depend on regulations.	2002				
Prevent active ecological	Groundwater at groundwater/surface water interface, surface water at areas where	ITRC 2006f, 2011b				
exposure via soil/	groundwater/surface water discharge has been indentified, shallow groundwater within					
sediment, soil gas, and/or	rooting depth, and/or contaminated sediments in surface water should be monitored for					
groundwater	VOCs.					
	Soil gas in the soil profile where soil-dwelling organisms reside should be monitored for	Archibald, Hull, and				
	VOCs to determine impact to food chain and/or plant uptake (lethality).	Diamond 2007				
Prevent adverse work	All media should be considered for work exposures to VOCs, including but not limited	USACE 2008; ITRC 2007c,				
related exposures via	to odors, indoor air, direct contact with soil/sediment, and/or soil gas.	2007d				
soil/sediment, soil gas,						
and/or groundwater						
Extent						
Prevent expansion of	Monitor the groundwater from source area and plume perimeter wells. Based on plume	ITRC 2010b, NAVFAC				
source zones and plumes	boundaries and monitoring type, select monitoring locations (upgradient, cross gradient,	2008, USEPA 2004				
	downgradient, and within plume treatment zones). Then, perform trend analyses to					
	determine whether the plume is expanding, contracting, or at steady state as a result of					
	remedy(ies).					
Reduce the extent of	Sample soil and groundwater to evaluate potential remedies. Once the extent of the	ITRC 1999, 2004a, 2005a,				
source zones and plumes	plume is understood, impact to the extent can be evaluated (see Section 5.5). Options for	2005b, 2006а–е, 2007а,				
	evaluation include CSM, statistical analysis, and modeling.	2008b; USEPA 2008				
	Longevity					
Reduce the period in	Assessing the longevity of the source zone and plume is based on time series data.	ITRC 2010b, USEPA 2008,				
which immobile	Several simple source decay models can be used to predict and track the progress of	Chapelle et al. 2003				
contaminants in source	immobile contaminant attenuation. The CSM should be updated at least annually to					
zones and plumes will	track changes in contaminant mass and concentration over time. In addition, mass					
provide persistent	flux/discharge measurements can provide an understanding of the strength of the					
releases to groundwater	contamination (be it source or plume).					
and/or soil gas						

Table 5-1 Resources	for monitoring	remediation of	chloringted	solvents
$1 \text{ abit } 5^{-1}$. Resources	tor momenting	remember of	unormateu	SOLVEILD

5.4.2 Mass

Estimating the mass of a contaminant, either removed, reduced, destroyed, or remaining, from a chlorinated-solvent plume (source zone or downgradient plume) can be an effective way to evaluate remedial performance and assess potential exposure. Estimating mass destroyed can be derived from calculating the total mass balance, including the degradation products, or measuring the difference between the estimated initial and final aqueous mass. ITRC (2010b) points out:

Many regulatory discussions about sites with groundwater contamination are driven by point-in-time measurements of contaminant concentration—snapshots of contaminant concentrations that may appear to be relatively stable or to show notable changes over time. However, concentration data alone cannot answer all questions critical to contaminant plume assessment or management.

Use of DNAPL mass, either removed or remaining, in predicting remedial success may be difficult due to uncertainties in estimates.

5.4.3 Mass Flux/Discharge

Recent research efforts and remediation activities have begun to avoid total reliance on contaminant concentration in soil and water for site characterization and remedial performance assessment. Contaminant mass flux and mass discharge, in conjunction with contaminant concentrations, are used to better understand contaminant behavior and encourage more precise decisions on remedial activities (ITRC 2010b, SERDP/ESTCP 2010). Mass flux and mass discharge estimates can help remediation project managers answer several key questions:

- Is the contaminant plume stable, expanding, or contracting?
- How will a proposed remedial action affect the future distribution, transport, and/or fate of the contaminants?
- What will be the risks and exposures at various points throughout the foreseeable future?
- How much source removal will be needed before transitioning to other technologies such as ISB or allowing MNA to complete the site remediation?

These estimates do have limitations and inherent uncertainty (ITRC 2010b, Sections 2.5 and 4.5). In fact, the uncertainty can be significant and should be quantified and considered relative to the typically more uncertain "concentration only" approaches. The collection of mass flux and mass discharge data can increase cost, since reliable mass flux or mass discharge estimates often can require better local characterization of the hydraulic conductivity and groundwater flow than the information typically available for a site. The degree of accuracy required for mass flux or discharge estimates should be determined based on objectives. In some cases an initial rough approximation may be sufficient, while more accurate measurements are necessary later (ITRC 2010b). Even with the uncertainty found in these measurements, mass flux and mass discharge data may improve evaluation of remedial activities because they do the following:

- combine contaminant concentration and groundwater movement data
 - o can be conceptually linked to the dose-response curve used in exposure evaluation
 - o provide a new perspective on potential impacts to receptors
- quantify changes in contaminant mobility and movement over time
- enhance evaluation and optimization of remedial technology and system operation
 - o help in determining whether or when remedial goals will be approached or met
 - help in assessment of effectiveness or benefit of additional treatments over distance or time
 - provide additional insight and information on remedy response(s) within the aqueous phase (e.g., stagnant versus mobile aquifer)

5.5 Data Evaluation

Data evaluation and interpretation are key components to evaluate whether functional objectives are being achieved at a sufficient rate (i.e., Is performance of a remedial approach indicative of a successful outcome?). A variety of tools and methods can effectively synthesize data to establish whether progress towards objectives is being made, generally including updating the CSM, statistical analysis, and modeling, which can include predictive and validation modeling. The follow sections provide brief overview of these tools and methods, along with an example to illustrate how to evaluate progress towards achieving objectives as the platform for decision making.

5.5.1 Maintaining the Conceptual Site Model

Continued reassessment of the CSM is an essential element of an IDSS. Each type of monitoring used at chlorinated-solvent sites (compliance, process, and performance) is essential for ongoing verification and development of the CSM (see Chapter 2). Evaluation of data sets, through the use of multiple lines of evidence, supports strategic decision making, including remedy evaluation as described later in Chapter 6. The CSM should be updated each time functional objectives are assessed and as a monitoring program is implemented.

Advances in data processing have improved our ability to maintain and continuously update a site's CSM using data visualization. Data visualization has the following potential benefits:

- increased stakeholder engagement
 - o a three-dimensional image conveys more information than many two-dimensional images
- improved CSM
 - o improved understanding of the vertical distribution of contaminants
 - o assessment of simplified two-dimensional methods for consistency
 - o additional statistical analysis methods
- improved remedy design, cost effectiveness, and performance
 - o improved understanding of spatial position of residual impacts
 - o reduced quantities of treatment materials as a result of better contaminant targeting

Database and processing improvements have reduced the cost of data visualization in the last several years. Examples of visualization software packages and tools include the following:

- ArcGIS 3D Analyst
- EarthVision
- Groundwater Modeling System
- MVS (a Commercial Tech product)
- Google Sketch Up and Google Earth
- AutoCAD

5.5.2 Statistical Analysis

Evaluating statistical trends is one of the most useful methods for assessing monitoring data sets to determine whether progress is being made towards a quantitative objective (e.g., rate of reduction in groundwater contaminant concentration in compliance well). The latest version of the *Statistical Analysis of Groundwater Monitoring Data at RCRA Facilities: Unified Guidance* (EPA 2009b) is a compendium of current statistical methods in use at many chlorinated-solvent sites. Groundwater statistical methods are a continuously developing discipline, and ITRC formed a team in 2011 to develop additional guidance.

One of the most common statistical methods is trend analysis of the rate of change in a metric. Trends are very important to establish the rate at which a functional objective is being achieved and can be used predicatively to estimate the time required to achieve the objective. However, any predictions must be explained, and those explanations must be validated by continued data evaluation. There are a number of statistical and empirical methods to calculate and define trends. For example, Aziz et al. (2003) and the Monitoring and Remediation Optimization System (MAROS) present a method where Mann-Kendall analysis and/or linear regression is used to categorize time series data as having either an increasing, probably increasing, stable, probably decreasing, or decreasing trend or statistically "no trend" at all. Other tools such as SourceDK (see Section 5.5.3), GTS, and Summit Monitoring can also be used to determine trends.

Figure 5-1 illustrates a decision framework from which to begin the data trend interpretation process. The initial step is answering the question of whether a remedial action is being taken. From there, one is brought to either a set of blue contaminant trends indicating the plume is being remediated (increasing, stable [see Text Box 5-2], decreasing, or no trend) or orange trends indicating that the plume is not being remediated. After establishing the behavior of the

monitoring results from Figure 5-1, refer then to Tables 5-2 (plumes or aqueous phase) or Table 5-3 (source zone). Each table offers possible interpretations and types of decision needed based on the trend indicated in Figure 5-1. In addition to the decision framework tables, there are several key tools that can be used to evaluate trends, such as the MAROS software. MAROS is a database application developed to assist users with groundwater data trend analysis and long-term monitoring optimization at contaminated groundwater sites.

Text Box 5-2. Air Force Plant 44, Stable Trend Resulting in a Change in the Remedy (see Appendix A)

TCE values immediately below the former disposal areas indicated that mass discharge equaled mass removed using the P&T system. This finding resulted in the decision to remove the source areas while still operating the P&T system.



Figure 5-1. Plume or source treatment decision framework. See Tables 5-2 and 5-3 for details.

Table 5-2. Decision framework for interpreting groundwater plume trends (Monitoring location[s] is downgradient of a recently applied source remedy where primary contaminant concentrations in the adjacent groundwater plume are still too high. An asterisk [*] implies that additional monitoring at the leading edge of the plume is necessary for the recommended additional assessment.)

Is plume being actively	Trend of primary contaminant	Possible interpretations		Suggested action
treated?	concentrations Increasing	Source remediation increased mass flux into plume by changes in local hydraulic pressures, thermal conditions, and/or flow patterns.	•	 Assess whether remedy is creating issues. If so, adjust remedy. Assess whether additional mass is likely to be attenuated within the plume and remedy is protective of human health and the environment (HHE) and will meet objectives.* If not, implement other remedial activities at/or downgradient of the source area.
	Stable	Remaining mass is in localized equilibrium with groundwater, likely natural attenuation diffusion-controlled environment. Plume remediation is occurring, but timescale may now be longer than thought.	•	 Assess whether existing approach is protective of HHE and will meet objectives.* If not, consider implementing an additional or changed remedy and/or implement groundwater containment/administrative controls until remedial objectives are achieved.
Yes	Decreasing	Source flux is no longer dominating plume formation. Plume mass will be reduced by plume remediation and/or natural mechanisms.	•	 Assess whether rate of mass removal is likely to achieve objectives in reasonable time frames. Assess whether plume depletion rates will protect HHE.* If not, for either of the above issues, adjust the remedy or consider implementing an additional remedy. May consider switching to lower-cost/unit mass removal technology.
	No trend	Flux from source is periodically spiking to bring large, temporary, increases in plume concentrations. The source of these source area spikes is unknown. Data gaps are likely.	•	 Reconsider CSM/collect additional data. Assess whether existing remedy is protective of HHE and will meet objectives.* If not, consider implementing an additional remedy or implement groundwater containment/administrative controls until remedial objectives are achieved. Consider implementing/changing source treatment.

Is plume being actively treated?	Trend of primary contaminant concentrations	Possible interpretations	Suggested action
	Increasing	Plume is not at steady state and is expanding. Source remediation increased mass flux for reasons noted above.	 Assess whether remedy is causing issues. If so, adjust remedy. Then assess whether additional mass flux is likely to be naturally attenuated and whether remedy is protective of HHE and will meet objectives.* If not, implement additional remedy to further stabilize/treat source and/or contain/treat plume.
No	Stable	Source flux is no longer dominating plume formation. Plume mass is in localized equilibrium with groundwater, likely due to natural attenuation and diffusion-controlled environment, but time to reach objectives will be long.	 Assess whether natural attenuation is likely to achieve objectives in reasonable time frames and whether remedy is protective of HHE.* If not, implement a plume treatment technology and/or groundwater containment/administrative controls until remedial objectives are achieved.
	Decreasing	Source flux is no longer dominating plume formation. Plume mass may be reduced by natural mechanisms.	 Assess whether natural attenuation is likely to achieve objectives in reasonable time frames and is protective of HHE.* If not, consider application of a plume remedy to improve contaminant mass removal rates and/or adjust the source remedy and/or implement groundwater containment/administrative controls until remedial objectives are achieved.
	No trend	Flux from source is periodically spiking to bring large, temporary increases in plume concentrations. The source of these spikes is unknown. Data gaps are likely.	 Reconsider CSM/collect additional data. Assess whether existing remedy is protective of HHE and is likely to meet objectives.* If not, implement an additional remedy.

Table 5-3. Decision framework for interpreting source area trends (Monitoring locations are immediately downgradient or at the downgradient edge of the source area, where primary contaminant concentrations are still too high and no active plume remedy is in place. An asterisk [*] implies that additional monitoring at the plume's leading edge is necessary for the recommended additional

		assessmer	l.)
Is the source being actively treated?	Trend of primary contaminant concentrations	Possible interpretation	Suggested action
	Increasing	Source remediation increased mass flux into plume by changes in hydraulic pressures, thermal conditions, and/or flow patterns.	 Assess whether remedy is creating issues. If so, adjust remedy Then assess whether natural attenuation will likely control mass discharge increase, is protective of HHE, and will meet remedial objectives. If not, add an additional remedy. Maintain action or optimize if increase is primarily parent compound.
Yes	Stable	Remaining source mass is in localized equilibrium. Plume likely controlled by natural mechanisms, diffusion controlled, but the time to reach goals may be long.	 Assess whether remaining flux will likely be controlled by natural attenuation, will meet remedial objectives, and is protective of HHE.* Assess whether the likely time frames are reasonable. If not for any of the above, consider implementing a plume remedy and/or implement groundwater containment/ administrative controls to achieve remedial objectives.
	Decreasing	Source flux is no longer dominating plume formation. Plume mass may be reduced by natural mechanisms.	 Assess whether rate of mass removal will achieve objectives and is protective of HHE.* Consider switching to lower-cost/unit mass removal technology. If not, adjust the source remedy and determine whether stable conditions likely will be reached. If so, see that box.
	No trend	Selected technology not improving mass removal rates. Data gaps are likely.	 Reconsider CSM/collect additional data. Change and/or add a technology until conditions protective of HHE and the remedial objectives are reached.* If only stable conditions are reached, see that box.

assessment.)

Is the source being actively treated?	Trend of primary contaminant concentrations	Possible interpretation	Suggested action
	Increasing	Source material redistributing, nonstable source, and/or recent release. Data gaps are likely.	 Reconsider CSM/collect additional data. Assess whether the additional flux is likely to be attenuated within the plume. If not, implement remedy(ies) to stabilize/remediate source and/or initiate plume remediation.
No	Stable	Source mass in localized equilibrium. Likely a natural attenuation–controlled environment. The time to reach remedial objectives may be long.	 Assess whether a source or remaining flux meets remedial objectives. Consider more aggressive technologies and their cost/benefit to enhance diffusion/desorption of remaining mass. Consider groundwater remedy should be implemented.
NO	Decreasing	Source and/or plume mass are being reduced by natural mechanisms.	 Assess whether natural attenuation will achieve remedial objectives in reasonable time frames and is protective of HHE. If not, implement a remedy to improve mass removal rates and/or implement groundwater containment/administrative controls until remedial objectives are reached.
	No trend	Source mass reduction rate is at steady state, and/or source mass is in matrix with low diffusion. Data gaps are likely.	 Reconsider the SCM/collect additional data. Assess whether natural attenuation will result in stable or expanding plume and still meet remedial objectives. If not, implement an active remedy to meet remedial objectives and be protective of HHE.*

5.5.3 Models as Tools

Groundwater models have been used extensively in the past for assessing both compliance and performance monitoring. *Contaminant fate and transport models* (also called "solute transport models"), typically based on the advection-dispersion (A-D) equation, are commonly used to evaluate plume stability in terms of potential expansion and/or contraction. More specifically, model simulations are used to estimate downgradient chemical concentrations and mass discharge before and after a remediation program. *Source zone models* simulate source processes such as changes in source strength due to natural attenuation and remediation.

Table 5-4 outlines some of the groundwater models commonly employed by the environmental industry today. It should be noted this list is for information purposes and is not intended to capture all models. Table 5-4 provides information on whether each model should be used as a *source* or A-D *fate and transport* model based on the A-D equation (or both), its solution method (such as whether it relies on an analytical or numerical approach), a summary of the model's capabilities, and where to get the model (all models are public domain unless labeled "commercial software package").

For example, BIOCHLOR is an analytical groundwater flow and contaminant transport model based on the A-D equation developed as a screening tool to simulate remediation through natural attenuation. BIOCHLOR simulates biodegradation of dissolved chlorinated solvents using sequential first-order decay for reductive dechlorination. It has a simple source zone model to account for source attenuation over time.

REMChlor is a new analytical model that contains many of the same processes as BIOCHLOR but also includes a source zone model which allows users to simulate source remediation (e.g., inputting a desired amount of mass removal in the source zone) and a plume module that allows evaluation of active plume remediation (e.g., electron donor addition) over nine different time/ space combinations. The plume module is based on the A-D equation. BIOPLUME, BIOCHLOR, and REMChlor are all distributed and supported by USEPA.

Models such as RT3D and SEAM3D use a finite-difference numerical solution of the transport equation to solve the A-D equation. As an input to the numerical transport model, the groundwater flow equation must be solved using MODFLOW, which is also a finite-difference model. As the table shows, numerical models can simulate the same natural attenuation mechanisms as the analytical models; however, the user defines all aspects of the site's conditions and the attenuation parameters. RT3D and SEAM3D do not have formal source zone simulation models but rely on user input to account for change in source strength over time.

Some of the tools provide calculator-type capabilities to answer specific questions. BioBalance has two modules related to electron donor/electron acceptor supply and demand. The SourceDK tool has an empirical data extrapolation tool to evaluate remediation time frames and the uncertainty in these estimates. Both SourceDK and NAS estimate the time to remediation and the uncertainties associated with those calculations. In addition, both NAS and BioBalance provide estimates for plume stabilization length and time frames.

Model	Solution	Intended	Capabilities and access
BioBalance	Mass balance	Source and/	Evaluate natural attenuation canacity at site
Tool Kit	approach	or $A_{-}D$ fate	Includes four modules (source, competition
	approach	and transport	electron donor, and plume) and combines the
		and transport	modules for the final mass balance
			modules for the final mass balance.
	Applytical	Source and/	Este and transport of chloringted solvents (first
DIOCIILOK	Allarytical	or A D fata	order deepy)
	solution	of A-D fale	order decay).
NAC	Combination	Source and/	www.epa.gov/ada/csmos/models.num
INAS	Combination	Source and/	Includes infee main interactive modules to
		or A-D fate	provide estimates for distance of stabilization,
	and numerical	and transport	time of stabilization, and time of remediation.
	solutions	G 1/	www.cee.vt.edu/NAS
REMChlor	Analytical	Source and/	Fate and transport of chlorinated solvents (first-
	solution	or A-D fate	order decay). Allows user to remediate source
		and transport	and/or plume at different times and different
			locations. <u>www.epa.gov/ada/csmos/models.html</u>
BIOPLUME	Numerical	Primarily	Fate and transport via inputting site-specific
	solution (up to	A-D fate and	hydraulic and attenuation parameters.
	two	transport	www.epa.gov/ada/csmos/models.html
	dimensional)		
MT3D	Numerical	Primarily	Fate and transport via inputting site-specific
	solution (up to	A-D fate and	hydraulic and attenuation parameters.
	three	transport	www.scisoft-gms.com (typically used in
	dimensional)		commercial software package)
RT3D	Numerical	Primarily	Fate and transport via inputting site-specific
	solution (three	A-D fate and	hydraulic and attenuation parameters.
	dimensional)	transport	www.scisoft-gms.com (typically used in
			commercial software package)
SEAM3D	Numerical	Primarily	Fate and transport via inputting site-specific
	solution (three	A-D fate and	hydraulic and attenuation parameters.
	dimensional)	transport	_
SourceDK	Analytical	Primarily	Remedial time-frame decision-support tool that
	solution	source	can evaluate data using three tiers. Tier 1 relies
			on empirical data, Tier 2 uses a box model, and
			Tier 3 uses a process model. <u>www.gsi-net.com</u>

Table 5-4. Summ	ary of models u	ised in the enviro	onmental industry

Models should be selected based on their intended purpose and inherent assumptions. For example, while analytical solution-based models allow for quick assessment of a site, the assumptions built into analytical solutions often mean that simplifying assumptions must be made to apply these models. The assumption of a homogeneous groundwater flow field is the most common simplifying assumption when applying analytical fate and transport models. There

are several other key assumptions that must be acknowledged, including chemical and biological reactions (and source zone depletion) typically assuming first-order decay, local equilibrium, and linear sorption. All can make dramatic differences in simulation results and are often confused for one another (e.g., nonlinear sorption can be easily confused with rate-limited sorption).

Numerical fate and transport models offer the ability to model more complex conditions (e.g., groundwater pumping or changing flow over time) of a site but incur the added expense to obtain site-specific parameters and time required to develop, calibrate, and validate the model. Regardless of the type of model, sensitivity analyses should be employed for assessing the parameter(s) driving the model results and developing a range of possible estimates.

Overall, the IDSS Team believes that the models listed in Table 5-4 can provide useful decisionmaking information regarding the impact of remediation on source zones and plumes. As discussed in Section 2.4.2, USEPA's REMChlor model is a relatively simple but particularly useful tool for evaluating remediation options and for monitoring the progress of site remediation toward a site's functional objectives.

Recently, there has been a call by some researchers (Payne, Quinnan, and Potter 2008; Konikow 2011) to revaluate some of the basic assumptions and applicability of the A-D equation used in several of the models in Table 5.4, citing inaccurate underlying assumptions and inaccurate representation of actual hydrogeologic conditions in the subsurface. The IDSS Team had extensive discussion regarding two different viewpoints about this emerging theoretical issue:

- Traditional view: Other researchers have concluded while the A-D model may have some theoretical inaccuracies, the way it is applied in typical groundwater model projects does provide useful, reliable information to site managers. In a typical groundwater modeling project, dispersion has these characteristics: (a) it is used as a adjustment factor to help represent large-scale heterogeneity that has shaped the size and shape of the observed groundwater plume, and (b) it is often a "second-order process," one that is much less important than advection and degradation for many modeling projects. In addition, while groundwater models without a matrix diffusion term do not account for this important process, skilled modelers now know that the A-D model may be too optimistic when simulating long-term, lower-concentration cleanup scenarios. This knowledge can be incorporated into site remediation strategies, particularly if the flexible site management approach shown in Figure 1-2 is employed.
- Alternative view: There are two sources of contaminant spreading in the A-D equation: spreading of molecules within the water mass (aqueous-phase diffusion) and spreading of the moving water mass within the porous medium (hydrodynamic dispersion). The spreading of molecules within the water mass (diffusion) is well-founded, and measured diffusivities are available for most compounds of interest. In retrospect, the hydrodynamic dispersivity element of the A-D equation requires turbulent mixing to impact spreading at the plume scale, but the pore dimensions and attainable velocities in aquifers assure us that only laminar viscous fluid flow is possible. In fact, field measurements repeatedly have shown that contaminant spreading in aquifers is very limited in the transverse (vertical and horizontal, perpendicular to the flow path) and longitudinal (along the flow path) directions.

The alternative view is that the limited spreading that does occur primarily depends on variations in aquifer permeability along the flow path and on pore-scale diffusion processes (e.g., Gilham et al. 1984), as compared to the assumption that hydrodynamic dispersivity (random-walk dispersion) more strongly influences transport in aquifers. Therefore, any groundwater model that incorporates significant hydrodynamic dispersivity overstates the potential for plume spreading and the resulting dilution. Models that rely on the A-D equation should be used with great caution or not used at all. (Text Box 5-3 provides a description of this viewpoint.)

Text Box 5-3. Viewpoint of One Groundwater Scientist Who Questions the Applicability of Advection-Dispersion Models ("Alternative View")

The ability of quantitative models to predict plume development and response to remediation has been severely tested in DNAPL sites and at research sites where solute transport has been studied at high resolution (Eggleston and Rojstaczer 2000). In particular, mathematical and conceptual limitations of the A-D equation, which is the foundation of many models, are now being recognized (e.g., Konikow 2011; Eggleston and Rojstaczer 2000; Payne, Quinnan, and Potter 2008). One way to illustrate the modeling difficulties is the predictions generated for a pulse of solute entering an aquifer as in a tracer study.

The upper portion of Figure 5-2 shows two concentration-versus-time tracer breakthrough curves. On the right is a Gaussian (bell-shaped) curve with its peak arrival time determined by the average groundwater velocity. This is the breakthrough curve that is predicted by typical applications of the A-D equation (a.k.a. ADE) approach. To the left is a log-normal peak that represents diffusion-based tracer behavior, and there are two key distinctions relative to the A-S prediction: (a) the peak arrival is much earlier than predicted by the average groundwater velocity due to the fact that groundwater flow is focused in the most permeable portion of the formation, and (b) the peak shows long tailing due to at least two factors: the observation well may be compositing multiple conductive zones (as described earlier in Figure 2-7) and diffusive migration of solute into and back out of lower-permeability strata adjacent to the high-flow groundwater pathways.

The lower portion of Figure 5-2 shows predictions related to the impact of source depletion or elimination on a dissolved-phase plume. The gray-line curve to the right side of the figure shows the predicted concentration reduction predicted with an A-D-based calculation. The cleanup front is a Gaussian curve, and its arrival time is estimated by the average groundwater velocity. Heterogeneities in natural aquifers lead to a different breakthrough of the cleanup front, depicted on the left curve of the lower panel in Figure 5-2. In this case, the initial indication of clean water transport occurs much earlier than the average groundwater velocities indicate. However, the tailing effect due to diffusivity and multivelocity effects shows as a tailing of the cleanup curve. The shape of the tailing process is determined in part by the nature of aquifer heterogeneities and the duration of contaminant exposure to the aquifer matrix.

When modelers using the A-D equation encounter early-arriving log-normal concentration patterns, they call it anomalous behavior (Konikow 2011) even though it is actually typical site behavior. This point gets to the heart of the difficulty that mathematical models encounter in real aquifer systems: actual site behaviors are "anomalous" in the Gaussian (A-D-based) model system. Konikow (2011) provided an analysis of the mathematical limitations of A-D-based models, and among the points he raised is the fact that the error-to-signal ratio becomes large when dissolved-phase plume concentrations fall to <1% of source zone concentrations. That means for a DNAPL-sourced plume, the models begin to generate unreliable predictions of leading-edge contaminant concentrations of 100s to 1000s of μ g/L, which means the predictions are unreliable over a large portion of the dissolved-phase footprint.

Site characterization practices have evolved dramatically in the past 5 years, and there is a rapidly increasing base of high-resolution source and plume mappings, as discussed in ITRC 2010b. The higher-resolution mappings show that aquifers are heterogeneous and anisotropic, as a rule, and that the scale of heterogeneities is sufficiently small in many cases to render aqueous-phase diffusion a relevant process. Consequently, there is a growing number of groundwater scientists who recommend that modeling practices be adjusted to represent contaminant transport with much finer-scale discretization

(allowing diffusivity to be correctly represented), use of de minimus hydrodynamic dispersivities (representing values obtained in numerous field research studies), and incorporation of realistic anisotropy and heterogeneities (populate the full nine-element permeability tensor to reflect actual site structure in ModFlow, for example). All would contribute to more realistic and reliable modeling.

Figure 5.2. Comparison of tracer breakthrough (upper graph) and cleanup curves from advection-dispersion based (gray lines) and advection-diffusion based (black lines) solute transport. The upper graph shows typical field tracer breakthrough in the solid black line. It is log normal in shape, with the tracer peak arriving at a time earlier than would be expected based on average groundwater velocity calculations. The bell-shaped (Gaussian) curve (gray line on the right side of the upper graph) depicts the tracer breakthrough behavior predicted by an A-D model calculation. Notice that the peak arrival time corresponds to the average groundwater velocity. The lower graph contrasts expected cleanup concentration profiles (concentration downgradient from a DNAPL source zone that has been completely eliminated) for the typical field site and an A-D model. The model (gray line)



projects a clean-water front arriving at a time corresponding to the average groundwater velocity, while a typical heterogeneous site (black line) is expected to show initial concentration reductions much earlier due to flow through the highest-permeability strata. The typical site cleanup curve is expected to show contaminant concentrations lingering much longer (tailing) due to diffusive contaminant mass exchange between zones of high and low permeability. *Source:* Redrawn from Payne, Quinnan, and Potter 2008.

While the IDSS Team had members representing both views, the overall team opinion was that the models in Table 5-4 should be a part of the IDSS guidance document and, when used correctly, can provide useful information to site managers. The spirited debate between these two viewpoints continues, while increasing our overall understanding of effective integrated DNAPL site strategy developments.

5.6 Monitoring Optimization

Monitoring programs should be routinely reviewed and optimized (ITRC 2004a, USEPA 2005a) to ensure that the data being collected continue to be useful and relevant in gauging achievement of site-specific functional objectives. As remediation progresses and geochemical conditions change, the monitoring program should be adjusted to collect the information most appropriate to evaluate the performance of the remedy, progress of the remediation, and character of the geochemistry.

Typical modifications to an established monitoring program consider the elements bulleted below within the context of reducing costs while still collecting the appropriate data to assess the remediation progress and geochemical conditions. To facilitate the optimization process, decision criteria for reducing frequency and/or removing locations and constituents should be explicitly stated in the monitoring approach prior to the onset of monitoring. This step helps establish expectations for all concerned parties.

- Monitoring network—Where to collect data depends on the sampling types (performance, compliance, and process) and their functional objectives. Process data should be collected as part of a dynamic O&M plan, which allows for sampling frequency, duration, and constituent alteration based on the treatment system's performance. A performance monitoring network at a chlorinated-solvent site typically changes over the life cycle of a treatment system and when transitioning from one remedy to another. Compliance monitoring networks should change as plume extent changes. Evaluation of the monitoring network is recommended on an annual basis. If the information gained at a monitoring point does not contribute to the functional objectives for that sampling type, then it may be appropriate to discontinue use of that monitoring point (NAVFAC 2010a).
- Frequency and duration of sample collection—Monitoring frequency and duration can depend on a variety of items such as seasonal variability, data trends, transient site conditions, and monitoring point type. Initially, four rounds of quarterly sampling are typically collected at monitoring locations to address items such as seasonal variability. Process monitoring may require more frequent monitoring to assess treatment system performance. Once a minimum of four data points is collected, trend analysis can be performed. Monitoring locations and constituents should be assessed against decision criteria and functional objectives to determine whether the duration or frequency of data collection should be changed. For example, decision criteria can define which monitoring frequency can decrease once stable or decreasing data trends are observed at the site.
- Contaminant-constituent monitoring—Analyte selection may change over time as the geochemistry of the site changes, as the remedy moves from active to passive (e.g., ISCO to

MNA for metals mobilization), and as contaminants are no longer COCs. These changes in the life cycle of the project can provide significant costs savings if the ability to optimize the monitoring approach is incorporated when writing the monitoring plan.

In addition to traditional statistical methods, several software tools are available to help optimize monitoring approaches. For example, MAROS, GTS, 3TMO, and Summit Monitoring are specifically designed for monitoring network optimization through spatial and temporal sampling reductions. These tools are focused on reductions in long-term monitoring programs. Section 5.7 illustrates the development of a monitoring approach for the Washington Square Mall example (Section 2.5).

5.7 Developing a Monitoring Approach Example Site

The monitoring program supporting an IDSS must be dynamic by nature through the project life cycle. The following example illustrates the development of a monitoring program from functional objectives. Such a monitoring program should be routinely evaluated with respect to the functional objectives to identify when new or revised functional objectives are needed and when sites achieve important milestones that suggest other elements of the IDSS should be reevaluated to maximize the efficiency and value to the site management program.

Figure 5-3 shows the process for developing a monitoring approach for the Washington Square example site. The first step, describe the absolute and functional objectives for the site, is illustrated in Chapter 3, Table 3-3. Section 4.4 describes the second step, identify the selected remedies for the site. The remedy consists of soil removal for the unsaturated source zone and ISCO using permanganate for the saturated plume zone. Step 3 identifies the location, type and quality of samples, techniques, and measurements needed to provide data. The data will be used to assess a remedy's progress towards achieving its functional objectives. In Table 5-5, the monitoring media, monitoring method, and monitoring location columns are completed based on data and information necessary to evaluate progress towards the functional objective.

In Step 4 the monitoring frequency should be adequate to detect changes in the geochemical conditions and remedial progress at the site. Monitoring frequency varies with site-specific conditions but should be adjusted for evolving monitoring requirements over the life of the remedy. While that frequency may be greater than is typically employed, it should be realized that the higher frequency is required to obtain the data to make informed management decisions while the remedial action is occurring and the frequency can change over the lifetime of a remedy. For example, weekly monitoring may be required during an ISCO treatment, but quarterly monitoring may be used after the treatment to monitor the long-term aquifer response to the treatment. Table 5-5 lists the overall monitoring period as well as potential monitoring frequencies, such as weekly, monthly, or quarterly. For example, monitoring frequency may be decreased if it is determined a remedy is performing as expected and very little change is observed from one monitoring period to the next, or it may be increased if unexpected conditions occur or the effects of remedy modification need to be observed more frequently.



Figure 5-3. Developing a monitoring approach for the Washington Square Mall example site.

The fifth step is to identify how long monitoring will take place. Again in Table 5-5, the monitoring will take place for 24 months since this was the time frame established for achievement of the SMART functional objectives in Table 3-3. For many remedies involving restoration of groundwater to beneficial use, the monitoring period extends past that point in time when groundwater cleanup levels are achieved and the remedy is shut down to verify the exposure threat is eliminated and demonstrate "rebound" will not occur. This period of time is usually determined by regulatory authority.

Al	Absolute objective #1: Protection of human health and the environment										
	Functional objectives ^a	Monitoring media ^b	Monitoring method ^c	Monitoring location	Monitoring period ^d	Monitoring metric ^e					
1.	Vapor intrusion pathway (soils):	Soil gas, soil	Attenuation factor or	Under proposed	6 months; post-	40 µg/kg PCE for soil					
	Reduce concentrations of volatile		modeling based on	construction site	excavation	samples; µg/m ³ for soil					
	organics in the vadose zone that		site-specific		confirmatory soil	gas samples; reduction in					
	will allow a "no further action"		conditions used to		sampling	mass loading from the					
	determination for unrestricted use,		predict indoor air			source zone to the plume					
	with no administrative or		concentration; soil			(mass loading ≤ 2 OoM);					
	engineering controls required for		grab samples			regulatory soil cleanup					
	the soils within 6 months (vapor					goals					
	intrusion indoor air objective)										
	Metric: 40 µg/kg PCE highest measured residual concentration, an approximate 2 OoM reduction (1.0% residual)										
2.	Vapor intrusion pathway	Groundwater	Attenuation factor or	Under proposed	18 months	8 μg/L PCE: measure					
	(groundwater): Reduce	(transmissive	modeling based on	construction site		TCE, dichloroethene					
	concentrations of volatile	zone)	site-specific			(DCE), VC, ethene					
	organics in the groundwater that		conditions used to			degradation rates and					
	will allow for "unrestricted use"		predict indoor air			trend, also total organic					
	of the property, with no		concentration			carbon, Eh, pH; reduction					
	administrative or engineered					in mass loading from the					
	controls, within 18 months					source zone to the plume					
	(protection against vapor					(mass loading ≤ 2 OoM);					
	intrusion objective)					$g/m^2/day, \mu g/L$					
	Metric: 8 µg/L PCE highest measu	ured concentrat	ion, an approximate 2	OoM reduction							
3.	PCE loading to the aquifer:	Soil and	Mass flux	Source zone on-	24 months:	Reduction in mass loading					
	Reduce concentrations of PCE in	groundwater	measurement method	site plume	groundwater—could	from the source zone to					
	the vadose zone to eliminate/	(transmissive	of choice to measure	transmissive	be weekly, monthly,	the plume (mass loading					
	prevent further discharge of PCE	zone)	plume discharge	zones; boundary	quarterly; soil—	≤ 2 OoM); regulatory soil					
	into the underlying aquifer		reduction; active or	between source	post-excavation	cleanup goals; g/m ² /day,					
	(prevent loading to the		passive groundwater	zone and on-site	confirmatory	µg/L, mg/Kg					
	groundwater plume, stabilize and		sampling from	plume; source	sampling						
	eliminate the groundwater plume)		source zone and on-	zone low-							
			site plume; soil grab	permeability							
			samples	sorbed zone							
	Metric: 45 µg/kg PCE highest med	isured residual	concentration, an appl	Metric: 45 µg/kg PCE highest measured residual concentration, an approximate 2 OoM reduction (1.0% residual)							

T-LL F F CMADT for after all all	· · · · · · · · · · · · · · · · · · ·		C Mall
1 able 5-5. SIVIAK 1 functional of	jectives and monitoring	approach for wasnington	Square Mail

Absolute objective #1: Protection of human health and the environment								
Functional objectives ^a	Monitoring media ^b	Monitoring method ^c	Monitoring location	Monitoring period ^d	Monitoring metric ^e			
4. PCE and degradation products in	Groundwater	Active—grab sample	Source zone and	24 months: could be	State and/or federal			
the aquifer: Reduce	(transmissive	for immediate use;	on-site plume	weekly, monthly,	background, drinking			
concentrations of volatile	zone)	consider passive	transmissive	quarterly;	water, or commercial/			
organics in groundwater to		sampling for long-	zones	monitoring interval	industrial standard; µg/L			
background concentrations or		term monitoring		should support trend				
drinking water quality in 2 years,				analysis and prevent				
allowing for no restrictions on the				unnecessary				
ability to use the water				exposure risk if				
				contingency enacted				
Metric: Background or drinking water standard								

^{*a*} See Table 3-3.

^b Soil/sediment, soil gas, or groundwater.
^c Refer to Table 5-1.
^d Depending on the type of monitoring, may be dictated (regulatory compliance) or modeled (predictive).

^e For example, $\mu g/L$, mg/kg, $g/m^2/dy$.

Concentration in aqueous-phase equivalents (OoMs) from Table 2-4:							
$0 = >1 \ \mu g/L$ in aqueous-phase	$1 = >10 \ \mu g/L$ in aqueous-phase	$2 = >100 \ \mu g/L$ in aqueous-phase	$3 = >1000 \ \mu g/L$ in aqueous-phase				
equivalent	equivalent	equivalent	equivalent				

To summarize; the Washington Square Mall has been characterized (Chapter 2), the remedial functional objectives have been defined to accommodate the attributes of SMART (including the addition of interim functional objectives, Chapter 3), technologies have been selected and performance expectation defined (Chapter 4), and a monitoring approach has been established that defines the media in which to monitor the preestablished metric, the method(s) used to monitor the metric, the location of the monitoring system, the initial monitoring period or interval, and the initial duration of monitoring (Chapter 5). What remains is what most project managers find most troubling and where most site remediation projects unravel. In Chapter 1 the fifth key area of this guidance

reevaluating the strategy repeatedly and even modifying the approach when objectives are not being met or when alternative methods offer similar or better outcomes at lower cost

requires attention to several rather simple questions:

- Are your functional objectives being met?
 - Is progress toward functional objectives acceptable?
- Can objectives be achieved with greater efficiency?
- How do you troubleshoot the remedy if objectives are not being achieved?

Simple questions, yet few sites have developed an IDSS from the initial discovery of the site and consequently have not adequately addressed one or more of the first four keys areas discussed in Chapters 2–5. Returning once again to Chapter 1, to "…maximize the chances for successful outcomes related to chlorinated-solvent site management and cleanup," a site needs to have the following:

- a **conceptual site model** based on reliable characterization methods and an understanding of the subsurface conditions that control contaminant transport, reactivity, and distribution
- **remedial objectives** and performance metrics that are clear, concise, and measureable
- **treatment technologies** applied in sequence or in parallel designed to optimize performance and take advantage of potential synergistic effects
- **monitoring strategies** based on interim and final cleanup objectives, the selected treatment technology and approach, and remedial performance goals

Using the Washington Mall example, this guidance has illustrated the keys points in each topic that experienced practitioners, consultant, and regulators can use to manage a chlorinated solvent–contaminated site. Before going into the fifth and final key point from Chapter 1, review Appendix B, which illustrates the entire approach to developing an IDSS using another, more complex example. This appendix enables readers to follow an illustration of all the key points of Chapters 2–5, uninterrupted, using a single example.

Following review of the Appendix B example, Chapter 6 describes an approach to evaluate progress toward functional objectives and make positive decisions about the remedy, CSM, and remedial objectives.

6. **REMEDY EVALUATION**

Evaluating the remedy and key decision points during implementation of an IDSS involves answering rather simple questions:

- Are the functional objectives being met?
 - Is progress toward the functional objectives acceptable?
- Can objectives be achieved with greater efficiency?
- How do you troubleshoot the remedy if objectives are not being achieved?

This chapter describes the reevaluation of a remedy when progress toward functional objectives is not acceptable. Practically, most sites at which an IDSS is under consideration are at a point where the remedy is not making acceptable progress towards achieving the functional objectives (Section 6.1). Currently, reevaluation of these sites often focuses on technology application without also reevaluating whether the CSM or the absolute and functional objectives are impeding measureable progress. The process model provided in



this chapter includes consideration whether, even if progress *is* being made toward achieving functional objectives, optimization of the strategy is warranted to achieve success most effectively (Section 6.2). The process model also outlines steps for reevaluating a site, including addressing inadequate CSMs (Section 6.3.1), functional objectives (Section 6.3.2), or the remedial technologies (Section 6.3.3).

6.1 Evaluate Whether Objectives Are Being Met

Periodic reviews of the data and the overall strategy are generally required (e.g., 5-year reviews under the CERCLA process) and should be conducted with any long-term remedy. A variety of tools and methods can effectively synthesize data to establish whether progress towards objectives is being made, as discussed in Chapter 5. The timing of a remedy review varies depending on the expected objectives and anticipated remedial rates and outcomes. For instance, if a remedy is intended to last 20 years, 5-year reviews may be sufficiently frequent for evaluation, optimization, and troubleshooting. However, the timing of reviews must be sufficiently frequent to allow for the contingency to alter the plans or remedy if not performing as expected. For instance, if the remedy includes source treatment to reduce contaminant mass discharge within 5 years, a 5-year review does not provide sufficient time to troubleshoot the source treatment. The review may be comprehensive (e.g., CERCLA 5-year review) or may evaluate only one functional objective (e.g., whether source treatment reduced contaminant mass discharge within the first 5 years). Therefore, review periods must be consistent with the time frames of the functional objectives. Guidance that is helpful during these reviews includes AFCEE 2006, USACE 1999b, and ITRC 2004a.

Generally, performance evaluation of the remedy should identify changes that have occurred, remaining potential risks, and opportunities for improvement (i.e., optimization). It is important that the functional objectives are SMART, that sufficient and appropriate data are collected that directly support decision making regarding a specific functional objective (e.g., USEPA 2006 and 2005b outline procedures for aligning data collection strategies to objectives), and that the desired outcome is clearly understood and accepted. Table 6-1 describes examples of objectives described in Table 5-5 and provides examples of how those objectives might be evaluated, including time frames for performance review.

6.2 Remedy Optimization—Can Objectives be Met with Greater Efficiency?

An important component of a remedy reevaluation is investigating whether best practices have been implemented and whether the current practices are consistent with any new findings to ensure that the functional objectives are being pursued as efficiently as possible. There are often significant changes in site management over the course of a long-term environmental restoration process due to the dynamic nature of environmental law, ever-improving remedial technologies, and improved understanding of impacts of remedial actions (including green and sustainable practices). A decision to optimize the original strategy is typically based on a variety of site-specific factors:

- cost reduction, whether monetary, temporal, or sustainability-based
- changes in resource use (e.g., property transfer)
- potential incorporation of new technologies
- enhanced operation of an existing technology or system state-of-the-art practices

Technology optimization focuses on refining technology process operational parameters and controlling site conditions (e.g., injection or feed rate, soil or groundwater pH or Eh, etc.) to more closely match the requirements of the treatment and achieve functional objectives more cost-effectively (see Text Boxes 6-1 and 6-2).

Text Box 6-1. Caldwell Trucking, Optimizing In Situ Treatment (see Appendix A)

A full-scale field test using enhanced biological treatment from January 2001 to July 2002 was designed to determine whether enhanced bioremediation was viable to treat residual DNAPL in the basalt bedrock. The test goals were to accelerate the dissolution and treatment of source material and reduce the overall lifetime and impact of the source, rather than to achieve specific concentration reductions (NRC 2005).

Text Box 6-2. Test Area North, Optimizing In Situ Treatment (see Appendix A)

The results of abiotic column studies confirmed that the dissolution of TCE DNAPL was enhanced during amendment with high concentrations of some electron donors. Of these, a whey powder solution enhanced TCE DNAPL dissolution by a factor of 6 while sodium lactate had a much smaller impact (Macbeth et al. 2006).



A,	Absolute Objective #1: Protection of numan nearth and the environment								
Functional objectives		Monitoring	Monitoring	Monitoring	Monitoring	Monitoring matric	Review	Decision	
		media	method	location	period	Monitoring metric	period	Decision	
1.	Vapor intrusion pathway	Soil gas, soil	Attenuation	Under	6 months; post-	40 µg/kg PCE for	6 months	Rate of	
	(soils): Reduce		factor or	proposed	excavation	soil samples; µg/m ³		concentration	
	concentrations of volatile		modeling based	construction	confirmatory	for soil gas samples;		reduction in	
	organics in the vadose		on site-specific	site	soil sampling	reduction in mass		soils is	
	zone that will allow a "no		conditions used			loading from the		sufficient to	
	further action"		to predict			source zone to the		achieve the	
	determination for		indoor air			plume (mass loading		end point in 6	
	unrestricted use, with no		concentration			≤ 2 OoM); regulatory		months	
	administrative or		(ITRC 2007c);			soil cleanup goals			
	engineering controls		soil grab						
	required for the soils		samples						
	within 6 months (vapor								
	intrusion indoor air								
	objective)								
	Metric: 40 µg/kg PCE highest measured residual concentration, an approximate 2 OoM reduction (1.0% residual)								
2.	Vapor intrusion pathway	Groundwater	Attenuation	Under	18 months	8 μg/L PCE:	Monthly	Determine	
	(groundwater): Reduce	(transmissive	factor or	proposed		measure TCE, DCE,		whether rate	
	concentrations of volatile	zone)	modeling based	construction		VC, ethene		of	
	organics in the		on site-specific	site		degradation rates		concentration	
	groundwater that will		conditions used			and trend, also total		reduction in	
	allow for "unrestricted		to predict			organic carbon, Eh,		groundwater is	
	use" of the property, with		indoor air			pH; reduction in		sufficient to	
	no administrative or		concentration			mass loading from		achieve end	
	engineered controls,					the source zone to		point in 18	
	within 18 months					the plume (mass		months	
	(protection against vapor					loading ≤ 2 OoM);			
	intrusion objective)					$g/m^2/day, \mu g/L$			
	Metric: 8 µg/L PCE highest measured concentration, an approximate 2 OoM reduction								

 Table 6-1. SMART functional objectives, monitoring approach, and evaluation for Washington Square Mall

 Absolute Objective #1: Protection of human health and the environment

Absolute Objective #1: Protection of human health and the environment								
Functional objectives	Monitoring media	Monitoring method	Monitoring location	Monitoring period	Monitoring metric	Review period	Decision	
3. PCE loading to the aquifer: Reduce concentrations of PCE in the vadose zone to eliminate/prevent further discharge of PCE into the underlying aquifer (prevent loading to the groundwater plume, stabilize and eliminate the groundwater plume)	Soil and groundwater (transmissive zone)	Mass flux measurement method of choice to measure plume discharge reduction; active or passive groundwater sampling from source zone and on-site plume; soil grab samples	Source zone on-site plume transmissive zones; boundary between source zone and on-site plume; source zone low- permeability sorbed zone	24 months: groundwater— could be weekly, monthly, quarterly; soil—post- excavation confirmatory sampling	Reduction in mass loading from the source zone to the plume (mass loading ≤2 OoM); regulatory soil cleanup goals; g/m²/day, µg/L, mg/Kg	Quarterly	Determine whether the rate of concentration reduction in groundwater is sufficient to achieve the end point in 24 months	
Metric: 45 µg/kg PCE hig	hest measured i	residual concentr	ation, an appro	ximate 2 OoM re	duction (1.0% residual	l)		
4. PCE and degradation products in the aquifer: Reduce concentrations of volatile organics in groundwater to background concentrations or drinking water quality in 2 years, allowing for no restrictions on the ability to use the water	Groundwater (transmissive zone)	Active—grab sample for immediate use; consider passive sampling for long-term monitoring	Source zone and on site plume transmissive zones	24 months: could be weekly, monthly, quarterly; monitoring interval should support trend analysis and prevent unnecessary exposure risk if contingency enacted	State and/or federal background, drinking water, or commercial/ industrial standard; µg/L	Quarterly	Determine whether the rate of concentration reduction in groundwater is sufficient to achieve end points in 24 months	
Each stage (e.g., screening, evaluation, design, and implementation) of a response action can be optimized. Table 6-2 summarizes four optimization reviews. ITRC (2004a) published specifics on remedial process optimization, and a series of five brief ITRC guidance documents (ITRC 2006a–e) detail the key aspects of remedial process optimization.

Key questions to ask	Items evaluated	Best practice
Is the CSM current?	Existing CSM and site	Update the CSM with new
	understanding were based on the	assessment and remedial operations
	original site assessment and/or	data gathered since the CSM was
	initial remedial system	written or updated. Note: It is
	performance.	important to include "lessons
		learned" from both performing and
		underperforming remedies.
Are cleanup levels	Existing risk drivers, risk	Define cleanup goals clearly and
defined?	elimination or control strategies,	revise the IDSS based on revisions
	absolute remedial action	to CSM and changes to regulations.
	objectives, and cleanup goals.	
Can the system meet	Performance monitoring data,	Incorporate new monitoring and/or
the functional and	existing remedial design based on	interim goals as needed to improve
absolute remedial	planned performance expectations	evaluation of the performance and
goals?	(see Chapter 4), and emerging	progress of the technology. Evaluate
	remedial technologies to	when technology transition/change
	determine whether system can	is appropriate to meet remedial goals
	attain the functional and absolute	(functional objectives).
	objectives within the planned time	
	frame or more quickly and/or	
	cost-effectively.	
Can the system	Assess the remedial system	Adjust monitoring programs to
performance be	efficiency, in terms of time and	supply needed information to more
improved?	cost; the performance,	efficiently inform decisions about
	effectiveness, and monetary	technology optimizations and
	efficiency of the monitoring	technology transitions, and change
	program; and the estimated	system operations and incorporate
	operating life of both the remedial	new technologies that will improve
	technologies and the monitoring	remedial performance whenever
	programs.	practical.

 Table 6-2. Main elements for an optimization review

6.3 Remedy Evaluation

If project objectives are not being achieved at an acceptable rate or cost, the IDSS should be evaluated to determine whether one or more components of the strategy (i.e., CSM, functional objectives, or technology selection) should be revised. The three elements of the IDSS reevaluation process model are discussed below.

6.3.1 CSM Evaluation

The CSM (Chapter 2) incorporates all available assessment and remedial operations data into a single document. Given the comprehensive nature of a CSM, it usually takes more than one format to organize and display all the site information. CSM representations may include a text description supported by appropriate figures (e.g., site maps, cross sections, block diagrams, etc.), a release-transport-exposure depiction, and an exposure pathway analysis used to support the risk assessment (NAVFAC 2010b). Computer model simulations or exposure scenario models may be a component of the CSM but are not the entire CSM. Appendix C includes a CSM checklist that can be used to identify important elements of a CSM and determine whether elements are missing. CSMs are often used to do the following:

- organize project information
- obtain consensus about sources of uncertainty
- identify uncertainty that hampers decision making
- identify additional data collection needed either to reduce CSM uncertainties or to test CSM assumptions
- establish a single basis for all site decisions about risk, remediation, and reuse
- establish a basis for decisions regarding remedial cost-effectiveness and efficiency
- establish a basis for identifying decision units (i.e., area, volume, or a set of objects that is treated as a single unit for decision making)

Design and anticipated operations of the initial remedial system at any site are based on the original, primarily assessment-based CSM. The CSM can and should be revised throughout the different stages of a remedy, including remedial design and implementation, to improve the quality of the CSM and to ensure that essential information is included. Evaluating uncertainty in the CSM is critical and can help identify data gaps and actions that should be taken to reduce uncertainty in the CSM, thereby also reducing uncertainty in the project decision making. The CSM is a living document continually updated with additional investigation and lessons learned during remediation or on an expanding body of data gathered throughout the remediation (USEPA in press). Thus, the CSM "matures" throughout the project implementation, and as the quality of the CSM improves, so do decisions based on the accuracy of the CSM.

The CSM assembled from the findings of a remedial investigation (RI) often does not adequately portray the site conditions over time due to faulty or incomplete information, changing conditions since the RI (e.g., remedial actions), or the lack of essential information that is specific to a given remedial technology. An inaccurate or incomplete CSM can result in poor decision making, severely impacting both the duration and the cost of a remediation project. Deciding whether the CSM should be revised is aided by using the CSM checklist to decide whether essential elements are missing or inadequate (see Appendix C) and available tools, including hydrogeologic models, contaminant fate and transport models, and three-dimensional



visualization software that quantify the uncertainty in the site conditions. Table 6-3 summarizes these tools and whether they specifically include uncertainty analysis.

Model	Solution method	Intended application	Capabilities and access	Uncertainty
BioBalance	Mass balance	Source and/	Evaluate natural attenuation capacity at site.	
Tool Kit	approach	or A-D fate	Includes four modules (source, competition,	
		and transport	electron donor, and plume) and combines the	
		_	modules for the final mass balance.	
			www.gsi-net.com	
BIOCHLOR	Analytical	Source and/	Fate and transport of chlorinated solvents (first-	
	solution	or A-D fate	order decay).	
		and transport	www.epa.gov/ada/csmos/models.html	
NAS	Combination	Source and/	Includes three main interactive modules to provide	Yes
	of analytical	or A-D fate	estimates for distance of stabilization, time of	
	and numerical	and transport	stabilization, and time of remediation.	
	solutions	1	www.cee.vt.edu/NAS	
REMChlor	Analytical	Source and/	Fate and transport of chlorinated solvents (first-	Yes
	solution	or A-D fate	order decay). Allows user to remediate source	
		and transport	and/or plume at different times and different	
		1	locations. www.epa.gov/ada/csmos/models.html	
BIOPLUME	Numerical	Primarily	Fate and transport via inputting site-specific	
	solution (up to	A-D fate and	hydraulic and attenuation parameters.	
	two	transport	www.epa.gov/ada/csmos/models.html	
	dimensional)	r	<u></u>	
MT3D	Numerical	Primarily	Fate and transport via inputting site-specific	
	solution (up to	A-D fate and	hydraulic and attenuation parameters, www.scisoft-	
	three	transport	gms.com (typically used in commercial software	
	dimensional)	r	package)	
RT3D	Numerical	Primarily	Fate and transport via inputting site-specific	
	solution (three	A-D fate and	hydraulic and attenuation parameters, www.scisoft-	
	dimensional)	transport	gms.com (typically used in commercial software	
	unifolioitai)	umport	nackage)	
SEAM3D	Numerical	Primarily	Fate and transport via inputting site-specific	
SERINGE	solution (three	A-D fate and	hydraulic and attenuation parameters	
	dimensional)	transport	ny draune and allendation parameters.	
SourceDK	Analytical	Primarily	Remedial time-frame decision-support tool that can	
SourceDix	solution	source	evaluate data using three tiers. Tier 1 relies on	
	solution	source	empirical data Tier 2 uses a box model and Tier 3	
			uses a process model www.gsi-net.com	
Mass Flux	Analytical	Estimates	Estimates mass flux and discharge based on date	Ves
Toolkit	solutions	mass flux and	collected across a transect of a contaminant plume	105
TOOIRI	solutions	discharge	concered across a transeet of a containmant prante.	
Environmental	Numerical	Three	Three-dimensional visualization software with	Yes
Visualization	solutions	dimensional	restatistics to integrate site geologic	100
, iounization	(three	visualizations	hydrogeologic and contaminant data to provide	
	dimensional)	, isualizations	quantitative assessment of the quality of a site	
	(intensional)		investigation (min-max plume technology	
			confidence and uncertainty) and identification of	
			data gans	
			uuu zups.	

Table 6-3. Summary of models used within the environmental industry to develop CSMs
and evaluate uncertainty

If the CSM does need to be revisited, then it is necessary to identify specific data gaps and formulate activities to fill those data gaps. If not, then one should proceed to revisiting the functional objectives.

Common CSM inaccuracies

Chlorinated-solvent site CSMs are complex. Minor inaccuracies in one or more elements that affect the same subsurface element can interact multiplicatively, increasing departures from true subsurface conditions. Such inaccuracies occur most often in structure of the source area and plume and in geochemistry.

Structure of the source area and the plume requires a full understanding of all compartments where contamination exists to design an effective remedy. The distribution is dictated by the

factors discussed in Chapter 2. Where the contamination resides changes over time. The elements controlling subsurface transport and contaminant reactions (Section 2.2) within the source area and plume need to be periodically evaluated to assess whether adjustments to the remedy can improve the remedy effectiveness Text Box 6-3). Typical (See components of the CSM related to source and plume structure that can inaccuracies include cause the following:

Three-dimensional delineation— The depth, width, and length of the source and plume and the distribution of contaminants within the source area and plume often incomplete. are Threeinvestigations dimensional are often accomplished using vertical profiling with sensors on directprobes (e.g., membrane push interface probes) or with nested wells that collect continuous data or are screened and sampled over narrow intervals. These methods are particularly helpful when multiple water-bearing zones are impacted.

Text Box 6-3. Test Area North, Reevaluation of the CSM (see Appendix A)

The Test Area North CSM was developed through an iterative process of identifying data gaps, conducting activities to fill those data gaps, reporting on the results of those activities, and identifying new data gaps. This process resulted in a series of four reports. Following are examples of characterization activities that have been conducted in the source area since the sludge removal activity was completed and before the ISB field test was implemented:

- Several wells have been installed within or adjacent to the source area.
- Pumping tests, slug tests, and tracer tests have been conducted to determine aquifer properties, from which residual source distribution has been inferred.
- Standard geophysical, gamma spectroscopy and acoustic televiewer logging were performed in several source area wells.
- Cross-well seismic tomography was conducted.
- Extensive groundwater sampling has been conducted throughout the source area, both in support (see Section 2.3) and prior to initiation of ISB operations.
- Furthermore, results of abiotic column studies confirmed that the dissolution of TCE DNAPL was enhanced during amendment with high concentrations of some electron donors. Of these, a whey powder solution enhanced TCE DNAPL dissolution by a factor of 6 while sodium lactate had a much smaller impact (Macbeth et al. 2006). ISB remedy was initially implemented using sodium lactate injections and then optimized with whey injections.

These activities greatly improved the understanding of aquifer hydraulic conductivity, porosity, and preferential flow paths; dissolved contaminant composition and distribution; and residual contaminant source distribution.

- **Boundary conditions**—Hydrogeologic features that influence groundwater flow can include surface water, regional pumping wells, etc., all of which can change. For example, a pumping well may influence the direction and magnitude of groundwater flow, thereby affecting the contaminant plume structure, but may operate for only short intervals. It may be necessary to revisit discussions with local municipalities and residents about activities (e.g., groundwater pumping rates and additional or abandoned supply wells) that might cause conditions that influence contaminant fate and transport.
- **Surface features**—Buildings, slabs, impervious surfaces, vegetation, and other surface features impact infiltration, vapor transport, and groundwater flow; however, these features can change with time. These affect precipitation infiltration through vadose zone sources and contaminant leaching to the saturated zone, and water supply and flow in the upper groundwater. The CSM should periodically be updated to reflect these changes.
- **Multiple/alternative sources**—Unidentified sources (e.g., additional chlorinated solvent spills) or secondary sources (e.g., high-concentration contaminants in low-permeability lithologic soil units) can confound results. For this reason it is important not only to look closely at historical maps, figures, and production logs for potential sources, but also to ask site owners and operators about past practices.
- Unrecoverable NAPL source (Section 2.2)—Unrecoverable globs of NAPL trapped within pore spaces are difficult to identify and often impossible to recover. This residual NAPL can be an ongoing source of contamination and confuse monitoring results.
- Age and nature of the release (Section 2.4.1)—Catastrophic and slow releases can create sources and plumes with different structures. The maturity of the plume is also important when assessing how much of a role has been played by slow processes such as diffusion. Again, historical logs, documents, and site personnel may be helpful in better understanding the release history.
- **Geologic heterogeneity** (Section 2.3.1)—The permeability of geologic layers (i.e., stratigraphy) affects the lateral and vertical migration of DNAPL, contaminant distribution, and flow and transport of dissolved contaminants in groundwater. The site stratigraphy should be characterized from public knowledge of the regional hydrogeology and from boring logs collected during well installation and sampling. The latter are a direct source of site-specific information, but it must be remembered that the layers observed at one location are not necessarily competent throughout the site. Evaluating uncertainty in site stratigraphy using three-dimensional visualization models can help in identify data gaps.
- Matrix diffusion (Section 2.4.1)—Rock or fine-grained matrices can store significant quantities of contaminants both as free product and dissolved in "trapped" or immobile groundwater. Contaminant diffusion into the matrix makes it difficult to estimate the mass of contaminants and diffusion from the matrix (back-diffusion) and may extend the remediation time frame significantly. Plume age and the nature and extent of site geologic heterogeneity are very important in assessing the effect of matrix diffusion.

- Seasonal changes in hydrogeology—The amount of precipitation can influence the depth to groundwater as well as the flow direction and velocity. In addition, precipitation can dissolve and transport contaminants from the vadose zone to the groundwater plume. Hydrogeologic maps made from depth-to-water surveys of the site wells should be constructed at least once during the dry and once during the wet season to see whether there is a significant difference in groundwater elevation, gradient, and/or velocity and, therefore, plume direction and intensity.
- **Preferential pathways**—Higher-permeability zones or subsurface structures (e.g., pipelines, conduits, culverts, and sewers) can have significant impacts on contaminant transport. Information on such preferential pathways should be cross-referenced with the CSM to see whether they may influence groundwater hydraulics and/or contaminant movement.
- **Vapor-phase transport**—The potentially dangerous implications of vapor intrusion (Section 2.4.3) have become widely recognized, but vapor-phase transport can also transfer contaminant from a highly impacted groundwater zone to an otherwise unimpacted groundwater zone. For this reason, vapor-phase treatments such as SVE can be an important part of an IDSS.

Geochemical knowledge of the subsurface environment throughout the source and plume area is important in assessing appropriate technologies. The reaction mechanisms, extent, and rates of contaminant attenuation (including physical removal, sorption, diffusion, and abiotic and biotic destruction mechanisms) are dictated by geochemistry (e.g., redox conditions, pH, and alkalinity). For instance, if an aquifer is highly oxidizing, a technology that requires reducing conditions will likely be more difficult and expensive to deploy. Geochemical characterization can identify potential conditions that inhibit reactions (e.g., extremes in pH, high electron-donor demand, and high oxidant demand), as well as geochemical conditions that can cause chemical transformations of the contaminants. In addition, geochemistry can change significantly in different parts of the contaminant plume. Therefore, it is necessary to understand the variability in geochemistry.

Integral to the geochemistry are the microbiology and the potential for biotic and abiotic degradation of the contaminants. Potential degradation pathways are both a function of, as well as a major influence on, geochemical conditions in the environment. Parameters which can be monitored to assess contaminant attenuation mechanisms include the following:

- Daughter compounds containing fewer chlorine atoms than the compounds originally lost are evidence of breakdown.
- Presence of sources of carbon and energy for microbial metabolism. Individual contaminant compounds have degradation rates when alone that are different from those when the compound is part of a contaminant mixture (e.g., petroleum hydrocarbons or chlorinated solvents and petroleum hydrocarbons).
- Presence or absence of key microorganisms/genes known to degrade chlorinated solvents.
- Contaminant trends to see whether there is unexplained loss that may be due to abiotic mass destruction present for successful bioremediation.

6.3.2 Functional Objectives Evaluation

One key feature of an IDSS strategy is ensuring functional objectives meet the SMART attributes (Chapter 3). A fundamental component of this IDSS is to evaluate whether the functional objectives meet these attributes or need to be revised based on new information (e.g., a revised CSM). The functional objectives should be reviewed to ensure that the objectives are still consistent with other components of the IDSS (e.g., the CSM, employed treatment technologies, etc.). During this step of the troubleshooting process, any interim and final functional objectives will be reevaluated to achieve the following:

- determine whether they are comprehensive enough to achieve absolute objectives
- ensure that they are SMART (see Text Box 3-3)
- determine whether revision is necessary to align objective(s) with the revised CSM

Each functional objective should be evaluated to determine whether it is still appropriate for the revised CSM and can be met by the current remedial approach. Reevaluating the functional objectives begins with determining whether the functional objectives continue to accommodate SMART attributes. Adjustment can improve objectives that are ill-conceived for actual site conditions and available technologies. Ultimately, functional objectives that meet SMART criteria will support effective decision making throughout the implementation of the remedy. It is important to note that functional objectives are iteratively evaluated, with the CSM, to ensure that any new/revised understanding of site conditions is reflected in the functional objectives of the remedial action(s). Although certain functional objectives may not be revised due to compliance with promulgated regulations, many specific, interim objectives and/or process/ technology objectives can and should be revised during remedy implementation.

Some common issues with functional objectives include the following:

- Metrics do not align with functional objectives—Inaccurate or misapplied metrics can make achievement of the objective more difficult. Examples include applying (or expecting) residential standards in an industrial setting with no anticipated future change in the land use designation and not having an accurate understanding of the contaminant fate and transport and therefore using incorrect values for risk-based metrics. Selecting appropriate metrics that are consistent with the absolute objective (e.g., reduce risk to receptors) is key to establishing criteria that can be met.
- Unrealistic expectations regarding technology performance—Remedies for chlorinatedsolvent sites have often been developed with the expectation that one technology could achieve closure requirements, but experience has shown that those expectations are often unrealistic. In the field, active treatment technologies are often implemented with the expectation that passive treatment (generally MNA) will be sufficient thereafter. But MNA may not be allowed without additional active treatment and/or extensive testing, and the passive phase of treatment may be more costly and longer-lasting than expected. Fortunately, the database on real-world application is increasing, allowing managers to develop more realistic expectations (see Section 4.1.1).

- Data collected do not directly support functional objectives—Often, sampling and analysis plans include collection of data that do not provide information that is useful for evaluating whether the functional objectives are being met. Examples include using compliance or performance monitoring points that are far away from the remedial action (e.g., distant plume wells during source zone treatment).
- **Regulatory goals are not achievable in a predictable time frame**—Because it is often stringently required, one of the greatest challenges with chlorinated-solvent sites is regulatory compliance with MCLs. The time frame to achieve these objectives throughout the contaminated site can extend well beyond what can be reliably predicted (e.g., a human generation, or ~20 years, and it seems unreliable to predict beyond that time frame), even if active treatment is implemented. Instead, one or a series of functional objectives, which typically have much shorter durations, can "bridge the gap" between current conditions and the desired protective end point. These functional objectives allow managers to define success for partial remedies and to task and subtask success and monitor progress of remedial approaches many times during the overall treatment time frame.
- Lack of interim objectives—As discussed above, time frames for achieving compliance objectives may be so long that it can be considered impractical to conduct any treatment at all if it will not achieve the stringent absolute objectives. Interim functional objectives must be developed to measure and incentivize progress toward an absolute objective. For example, partial treatment may reduce risk to downgradient receptors to acceptable levels while leaving residual contamination on site. Establishing an interim functional objective of reducing the contaminant mass discharge (loading) to the plume to protective levels could provide an incentive for a partial source treatment.

6.3.3 Technology Evaluation

Part of troubleshooting a remedy includes evaluating the performance of an implemented technology if functional objectives are not realized at the desired rate and/or cost. As discussed in Chapter 4, several technologies can be applied to chlorinated-solvent sites, and the ability of any technology to achieve a given objective is highly site specific. Regardless of the technology selected and its application, the technology and its implementation must be reevaluated if the objectives are not being achieved.

If both the CSM and the functional objectives have been revisited and deemed appropriate (or revised as necessary), the currently deployed remedial technologies should be evaluated to determine whether other technologies/treatment trains may be more effective at achieving objectives. This technology evaluation may merely optimize the current technology or determine whether a new approach would be more effective or cost-efficient.

Many of the technology evaluation criteria developed in Chapter 4 are appropriate during the technology reevaluation. Generally, technology evaluation considers the following:

- Technology performance evaluation (Section 4.1)—Evaluate expected versus actual performance of the employed technology(ies) and the limitations that may or may not have affected performance.
- Technology performance expectations (Section 4.1.1)—Evaluate appropriate technologies for each of the 14 compartments based on the revised site understanding and the actual performance of technologies already employed (e.g., Sale and Newell 2011; Lebrón, Major, and Kueper 2008).
- Technology cessation/addition/transition—Compare the technology(ies) in use to other potentially applicable technologies, for example, containment versus removal (Sections 4.1.2 and 4.1.3). Determine whether and when to terminate a technology, add a technology, or transition from one technology to another (Section 4.2.2).

6.3.3.1 Technology performance evaluation

Technology performance is evaluated by comparing expected versus actual performance towards achieving functional objectives. During the performance evaluation, quantifiable metrics for media in each of the 14 compartments (e.g., soil, soil gas, and groundwater concentrations, molarities, or mass flux and mass discharge) are used to determine whether the remedy is making progress toward one or more functional objectives. In addition, technology-specific process performance objectives are evaluated to determine whether the technology is performing to specification(s). These data are used to make decisions regarding whether to do the following:

- continue operating and maintaining the existing technology/approach
- optimize the existing technology
- cease operation of the existing technology/approach
- transition from the existing technology/approach to another technology/approach

As discussed in Section 5.5, progress towards remedy objectives is often evaluated using data evaluation tools such as trend analysis and modeling. These tools can be used to map an expected performance or outcome of a treatment technology and evaluate progress towards that expected outcome. Since remedies for chlorinated-solvent sites often require multiple components to achieve the overall remedial (absolute) objectives, monitoring data should be evaluated to determine when to transition from one technology to another because a technology has reached a point of diminishing returns or has met criteria allowing a transition to another technology. The key to success is developing adaptive remedial strategies that allow for an iterative evaluation process and adjustment of the site strategy when beneficial. A National Research Council study describes adaptive management as "involving a decision-making process based on trial, monitoring and feedback ... and recognizing the imperfect knowledge of interdependencies existing within and among natural and social systems, which requires plans to be modified as technical knowledge improves" (NRC 1997).

Typical criteria used for performance evaluation and decision making for technology application (Section 5.5.1) include the following:

• Data trends—The rate of changes, e.g., concentration or mass discharge reductions over time.

- Point of diminishing returns—The rate of change has declined to a point where operation is highly inefficient (i.e., time-consuming and/or expensive compared to the benefits).
- No recognizable benefit—Treatment is occurring but is making little or no progress towards the functional objectives (e.g., source treatment is not causing further reductions in mass discharge to the plume, see Text Box 6-4).
- Best practices—The state of the practice of the original technology has been improved or other/better technologies have become available.

Text Box 6-4. Western Processing, Changing Direction after No Recognizable Benefit (see Appendix A)

After 8 years of aggressive efforts to restore the groundwater to acceptable levels via P&T and surface water infiltration, USEPA changed the remedy to containment in December 1995 for the following reasons:

- The chlorinated-solvent plume had a continual DNAPL source.
- O&M costs for the P&T system were prohibitively high.
- Monitoring showed that the plume was naturally attenuating outside the slurry wall.

Decision-making criteria regarding technology implementation, or termination, are important to a flexible, adaptive approach that considers all of the outcomes. Adaptive remedies have contingency plans for alternative approaches if the outcome is not as expected. Identifying a multicomponent remedy can streamline the remedial process by gaining acceptance for an approach to decision making that guides remedy implementation rather than specifying the use of technologies before the site is completely understood.

One useful criterion for determining when to transition technologies is the point of diminishing returns, which is often useful in deciding when an active treatment that requires inputs (i.e., energy, heat, amendments) is no longer providing cost-effective treatment. A related criterion is based on life-cycle analysis, which can be used to determine whether performance objectives are being approached at a sufficient rate (ITRC 2006d). Using data trends, life-cycle analysis can indicate the need for a transition between the original technology and a new technology or a suite of technologies. For example, the mass removal from a treatment zone over time (time trend) often exhibits a stable or asymptotic trend. Further enhancements produce little increase in removal, and other technologies may achieve similar results for less cost.

6.3.3.2 Operational decision points: adaptive strategies

As discussed by Sale and Newell (2011), an IDSS includes building a remedy by assigning technologies to the compartments and selecting technologies based on estimated performance (i.e., reductions in contaminant mass, flux, or discharge). Although this process provides a good conceptual understanding of the various compartments of a chlorinated-solvent site and potentially applicable technologies, the actual performance of a technology(ies) at a given site can be highly variable. Consequently, the IDSS includes an iterative remedy evaluation that identifies decision points. The predicted performance developed during technology mapping (Sale and Newell 2011) should be evaluated and the technology adjusted or replaced according to its actual performance at the site.

For instance, assume an order-of-magnitude reduction in contaminant mass discharge is used as the basis for selecting an aggressive treatment technology for the source zone. If the functional objectives have not been reached at the end of the planned treatment operational period, a decision must be made to do one of the following:

- continue aggressive treatment
- switch to a different technology
- cease operations and adjust objectives

To support this decision, process technologies can now be mapped with the new conditions and desired end points.

Once a system has been determined not to be meeting the design process objectives, the physical design of the remedy should be evaluated. Not only should the design assumptions be revisited but also design improvements such as changes to system operation (e.g., pulsing air sparging systems) and maintenance or replacement of equipment should be considered. New equipment may be selected due to lack of efficiency in older models, or changes to the remedial system may be made. If the current system cannot be improved to overcome the site limitations, remedy cessation and transition should be considered.

To illustrate the technology implementation decision points for a multicomponent strategy, a hypothetical example was constructed. Figure 6-1 illustrates a data evaluation for a hypothetical chlorinated-solvent site where the remedy includes aggressive treatment of a source zone followed by MNA. The overall objective of the source zone treatment is to reduce contaminant mass discharge from the source zone by 99% within 5 years. To achieve this objective, it is expected that aggressive treatment will reduce contaminant mass discharge by 90% within 5 months followed by transition to MNA to reduce mass discharge by an additional 9% over the next 4.5 years (see A of Figure 6-1). After aggressive treatment, performance is evaluated near the time of expected shutdown to decide whether the objectives have been met and whether the aggressive treatment can be discontinued. As shown in B of Figure 6-1, only a 60% reduction in contaminant mass discharge was achieved within the treatment time period instead of the desired 90%. Should aggressive treatment be halted on schedule or continued until the planned 90% reduction in mass discharged is achieved? Part C of Figure 6-1 compares the two options' impact on the overall objective of a 99% reduction in mass discharge. Without additional treatment, it will take MNA 6.5 years to achieve the functional objective. If this expanded time frame is acceptable, then the functional objective can be revised to achieve a 99% reduction in 7 years instead of 5, and aggressive treatment can be discontinued. If this revision is not acceptable, then a reevaluation of the remedy treatment options is necessary, including evaluating why the aggressive treatment did not achieve objectives—is it technology specific (e.g., it may be more difficult to extract mass stored in low-permeability zones) or due to issues with the CSM (e.g., there may be additional source material outside the treatment zone)? This example shows that several reevaluation points may be needed and different types of data may be appropriate for different decisions.



Figure 6-1. Hypothetical decision point illustrating expected outcome of an aggressive source treatment (A), expected and actual performance (B), and impact to the overall remedy (C).

6.4 Summary

Regardless of the difficulty of remediating chlorinated solvent–contaminated sites, there are numerous case studies demonstrating that the use of performance-based goals, combined with regular assessment and optimization of remedial activities, can lead to timely and cost-effective protection of human health and the environment. Examples of successful site management strategies contain case studies (USEPA 2009a Ryan 2010) that have either resulted in site closure or achieved remedial goals that have substantially reduced the remediation time frame and/or site management costs. However in some cases, despite best efforts, it may become apparent that the original objectives may not be attainable in a reasonable time frame. Examples of regulatory options available for these types of sites are provided on the "Regulatory Issues/ Challenges" page of the Mining Waste Treatment Technology Selection website (ITRC 2010a) at www.itrcweb.org/miningwaste-guidance/reg_issues.htm.

Thirty years has provided valuable insights into effective management and remediation of chlorinated-solvent sites. In essence, this IDSS guidance describes a process for developing an adaptive strategy for complex and dynamic chlorinated solvent DNAPL sites, which includes identification of key decision points to be periodically revisited, updated, and/or improved. This process includes identifying decisions points regarding when and how changes to the treatment strategy should be made. The adaptive elements of an IDSS include the following:

- an improved and living CSM that is updated throughout the remedy as new information becomes available and new decisions need to be made (Chapters 2 and 6)
- SMART objectives that relate specific performance criteria to actions (e.g., technologies that are periodically evaluated to ensure they continue to make acceptable progress and remain cost-efficient (Chapters 3 and 6)
- appropriate application of treatment options based on realistic expectations of performance and flexibility in technology transition when a point of diminishing returns has been realized or an alternative approach could achieve the objectives more cost-effectively (Chapters 4 and 6)
- iterative performance evaluation to determine whether acceptable interim progress objectives are being achieved or optimization or reevaluation of the IDSS is warranted (Chapters 5 and 6)
- an iterative approach to reevaluate the strategy and even change the approach when objectives are not being met or alternative methods offer the same or better outcome at lower costs or in less time (Chapter 6)

Although the IDSS does not provide easy answers, it does acknowledge the difficulties and compartmentalize the problem, enabling more effective site-management decisions. Accordingly, an understanding of all the elements can be gained by stakeholders that enable more effective decisions regarding how to manage sites. It is now recognized that management of a chlorinated-solvent sites is a lengthy process of site study, remediation, and post-remedial review. Some sites have contaminants remaining after the remedy is complete that require long-term monitoring and review.

The IDSS provides a means to improve monitoring and feedback mechanisms focused on crucial unknowns or uncertainties at the site and to revisit and adjust prior decisions, as warranted, in light of new information. In particular, the IDSS can improve information gathering and review in recognition of other important considerations, such as anticipated future uses of the site or remediation budgets and insurance options. Ultimately, the IDSS creates an accurate, comprehensive management model for sites at which chlorinated solvent occurs in multiple phases and is remedied using several methods over an extended period of time and under conditions of uncertainty and change.

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Appendix A

Case Studies

CASE STUDIES

Site Name	Page
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SITE NAME: DRY CLEAN USA #11502, ORLANDO, FLORIDA

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Site Description

Highlight included in Section 3.1:

Text Box 3-1. Dry Clean USA, Well-Defined Objectives

At Dry Clean USA the primary project goal was to see whether treatment could reduce PCE concentrations to the Florida MCL of $3 \mu g/L$ throughout the aquifer and to $30 \mu g/kg$ for soil (based on leaching potential) so that closure (i.e., no further action) could be obtained from the state regulatory agency.

Additional soil objectives (set by the state's drycleaner program) included 30 μ g/kg TCE, 400 μ g/kg cDCE, 700 μ g/kg *trans*-DCE, and 7 μ g/kg VC.

Having such well-defined objectives allowed the appropriate technologies to be applied and a Site Rehabilitation Completion Order was issued within 8 years of the initial treatment.

Dry Clean USA is a former PCE dry-cleaning facility that operated 1988–1998. The site is located in a shopping center in a mixed retail commercial/residential setting. Three public water supply wells are located within a 1-mile radius of the site. The shopping center was served by a septic system until the early 1970s. Soil sampling shows that the contaminant source areas appear to be the soil beneath the building floor slab where the dry-cleaning machine was formerly located and the sanitary sewer lateral line. The site was part of the Florida Department

of Environmental Protection's Drycleaning Solvent Cleanup Program. Investigation and cleanup occurred 1999–2005.

<u>Contaminant Nature and Extent</u>: PCE in groundwater was found to extend vertically to about 68 feet bgs. The dissolved-phase plume was found to extend 800 feet long and 300 feet wide. Contaminant concentrations before treatment included 27,300 μ g/L PCE in groundwater and 3.9 mg/kg detected in soil. The presence of DNAPL was suspected. The vapor intrusion pathway was not a concern at this site.

<u>Hydrogeology</u>: The site is underlain by a slightly silty, fine- to medium-grained sand to a depth of 47 feet bgs. This unit is in turn underlain by a 6-foot-thick, slightly sandy clay followed by a 20-foot-thick, fine- to medium-grained sand that is interbedded with clayey sand. A 4-foot-thick fine to coarse sand with shell fragments overlays a hard, phosphatic, limestone bedrock that occurs 93–94 feet bgs. The depth to groundwater is 8–10 feet bgs.

Lithology

- Slightly silty, fine to medium-grained quartz sands: surface to 47 feet bgs
- Slightly sandy clay: 47–53 feet bgs
- Fine to medium-grained sand interbedded with clayey sand: 53–83 feet bgs
- Sandy, clayey, silt: 83–89 feet bgs
- Fine to coarse-grained sand with shell fragments: 89–93 feet bgs
- Hard phosphatic limestone: 93–94 feet bgs

Conductivity

- Surficial (8–47 feet bgs): 1.4–2.4 feet/day
- Intermediate (47–93 feet bgs): 0.4 feet/day

Gradient

• Surficial: 0.002 feet/foot

Objectives

The primary project goal was to see whether treatment could reduce PCE concentrations to the Florida MCL of 3 μ g/L throughout the aquifer and to 30 μ g/kg for soil (based on leaching potential) so that closure (i.e., no further action) could be obtained from the state regulatory agency. Additional soil objectives (set by the state's dry-cleaning program) included 30 μ g/kg TCE, 400 μ g/kg cDCE, 700 μ g/kg *trans*-DCE, and 7 μ g/kg VC.

Remedial Approach

Technologies: ISCO (hydrogen peroxide), P&T, SVE

- SVE and P&T started in April 1999; chemical oxidation injection occurred October 4–5, 2005.
- SVE was chosen to remediate the soils at the site because it is a proven technology for recovering VOCs from permeable unsaturated sediments. Groundwater recovery was chosen to contain the contaminant plume and remediate contaminated groundwater.

- Low-level PCE concentrations in the source area well (installed beneath the facility floor slab and screened across the water table and the capillary zone) continued to persist, and the decision was made to polish contaminated groundwater using chemical oxidation.
- On October 4–5, 2005, an additional monitoring well was installed in the source area, and 1057 gal of a 1% hydrogen peroxide was injected into the former source area monitoring well.

Project Time Line

- 4/99—SVE and P&T systems start
- 12/01/00—SVE turned off
- 1/17/01—P&T system shut down
- 2/26/01—P&T system restarted because of rebound
- 11/02—P&T system turned off
- 10/04–05/05—Peroxide injections
- 2/07—Site Rehabilitation Completion Order signed

Performance

- SVE and P&T systems were run April 1999 to November 2002. The SVE system recovered at total of 9.8 pounds of VOCs; the P&T system recovered a negligible amount of VOCs.
- SVE for soil contamination and P&T for groundwater were successful in reducing groundwater contamination levels to $<10 \mu g/L$. Rebound did occur near the source area, so a 1% hydrogen peroxide solution was used as a polishing step.
- One year of post-oxidation groundwater monitoring (10/2005-10/2006) showed concentrations of PCE ranging from nondetect to 3 µg/L.

Remedy Evaluation

PCE concentrations in groundwater met cleanup target levels for four consecutive quarterly monitoring events 10/2005–10/2006.

<u>Costs</u>

- Assessment: \$97,700
- SVE/P&T systems: \$221,400
- Chemical oxidation: \$28,400
- Remedy O&M: \$147,800 (includes monitoring)
- Total: \$503,300

Outcomes and Challenges

The Site Rehabilitation Completion Order (no further action) was signed February 16, 2007, and all wells were abandoned.

Lessons Learned

• Numerical groundwater modeling was very valuable in siting the recovery well on location.

• The injection of a low concentration of a chemical oxidant in the upper portion of the surficial aquifer and the capillary fringe was successful in polishing already low concentrations of contaminants.

References and Links

- U.S. Environmental Protection Agency. 2009. DNAPL Remediation: Selected Projects Where Regulatory Closure Goals Have Been Achieved. EPA/542/R-09/008. www.clu-in.org/download/remed/542r09008.pdf.
- Also, a June 2008 site profile summarized by the State Coalition for Remediation of Drycleaners is available at <u>www.drycleancoalition.org/profiles/display.cfm?id=24</u>. Additional site-specific documents are referenced in the profile.

SITE NAME: WELL 12A SUPERFUND SITE, TACOMA, WASHINGTON

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Site Description

Well 12A is one of 13 wells used by the city of Tacoma to meet peak summer and emergency water demands. The well was taken out of operation by the city when it was found to be contaminated but has been operating since July 1983 with five airstripping towers. Investigations by USEPA found the source of contamination to be Highlight included in Section 3.2:

Text Box 3-2. Well 12A, Tiered Remedial Action Objectives

Tier 1: Address residual sources, including principal threat wastes, minimize the risk to receptors due to contaminated surface soils, and achieve at least a 90% reduction in contaminant discharge from the high-concentration source area to the dissolved-phase contaminant plume.

Tier 2: Achieve the cleanup levels at interim performance monitoring points.

Tier 3: Determine whether cleanup levels can be achieved in a reasonable time frame throughout the entire contaminant plume by discontinuing the groundwater extraction and treatment system operation and implementing MNA of remaining contamination.

If the Tier 3 compliance is deemed infeasible, additional remedial alternatives will be evaluated, and/or a technical impracticability waiver may be sought for the noncompliant portions of the aquifer.

centered on properties owned by the Burlington Northern Railroad and the Time Oil Company (see figure). A waste oil and solvent recycler had previously operated on the properties from approximately the 1920s until the 1960s. A groundwater extraction and treatment system (GETS) was installed in November 1988. Five additional GETS wells were installed in August 1993. During construction of an SVE system in August 1993, approximately 5,000 cubic yards of waste sludge was removed and 37,000 pounds of solvent was recovered by the vapor extraction system at the time of shutdown in May 1997. As of September 1998, the GETS had

removed 13,428 pounds of VOCs from treated groundwater. The GETS was not meeting the cleanup criteria set forth in the 1985 ROD. A remedial enhancement and optimization project was conducted to determine whether the groundwater extraction and SVE systems could be enhanced to address NAPL at the site or a different treatment technology would be more appropriate. Field work for the optimization project was completed in 2002 and resulted in recommendations to analyze the capture zone. Capture zone analysis was completed in 2005, and those being evaluated improve data are to the system (http://yosemite.epa.gov/r10/nplpad.nsf/88d393e4946e3c478825631200672c95/0c76d9e47c6c21 bf85256594006df0e7?OpenDocument).



Source: USEPA 2009.

Objectives

The remedy considered a final remedy for soils and an interim remedy for groundwater that will be protective, achieve RAOs, and assist in achieving the long-term objective for the Well 12A Site of restoring the aquifer to its beneficial use as a drinking water source for the City of Tacoma. Compliance with RAOs was divided into three tiers to allow for implementation of the multicomponent remedy and decision making, such as when to transition from one treatment technology to another and to O&M of the remedy. A brief description of each tier follows:

• **Tier 1.** The primary goals for the first tier of compliance are to address residual sources, including principal threat wastes; minimize the risk to receptors due to contaminated surface soils; and achieve at least a 90% reduction in contaminant discharge from the high-concentration source area near the Time Oil Building to the dissolved-phase contaminant plume. The soil excavation and disposal, in situ thermal remediation, and enhanced anaerobic bioremediation components of the remedy will be considered complete and the remedy considered operational and functional when the Tier 1 criteria have been met. This also will determine when operations transition to O&M.

- **Tier 2.** The primary goal of the second tier of compliance is to achieve the cleanup levels at interim performance monitoring points CW-1, CW-2, and Well 12A to ensure that groundwater concentrations are below ARAR (applicable or relevant and appropriate requirements)-specified levels
- **Tier 3.** The primary goal of the third tier of compliance is to determine whether cleanup levels can be achieved in a reasonable time frame throughout the entire contaminant plume, including the Time Oil Building source area, by discontinuing GETS operation and implementing MNA of remaining contamination. If the third tier compliance is deemed not feasible, additional remedial alternatives will be evaluated and/or a technical impracticability waiver may be sought for the noncompliant portions of the aquifer.

Remedial Approach

A comprehensive remedial action strategy was developed that includes aggressive treatment of persistent soil and groundwater contamination at the site, including primarily chlorinated-solvent DNAPL, LNAPL, and coal tars. Multiple treatment technologies will address different contaminated areas based on the nature and extent of contamination and risks to receptors within those areas. These areas include high-concentration soil and groundwater contaminated solvent contaminant plume that extends from the source area approximately 2000 feet to the east and approximately 2000 feet to the southwest to a municipal supply Well 12A of the city of Tacoma.

This multicomponent remedy (EPA 2009) includes in situ thermal treatment and excavation within the source area, enhanced anaerobic bioremediation in the high-concentration contaminant plume, operation of an existing groundwater extraction and treatment system, and well head treatment at the municipal supply well (see figure).

Performance

Pending—Implementation began in 2010.

Remedy Evaluation

Pending—Implementation began in 2010.

Outcomes and Challenges

Pending—Implementation began in 2010.



Source: USEPA 2009.

References and Links

- USEPA (U.S. Environmental Protection Agency). 2009. Amendment #2 to the Record of Decision for the Commencement Bay–South Tacoma Channel Superfund Site, Operable Unit 1, Well 12A, Tacoma, Washington. Region 10, Seattle. www.epa.gov/superfund/sites/rods/fulltext/a2010100003181.pdf.
- USEPA. n.d. "Commencement Bay–South Tacoma Channel," Region 10 Web page. http://yosemite.epa.gov/r10/cleanup.nsf/4c5259381f6b967d88256b5800611592/d3c814fe639 4c2ba882565220048abb2!OpenDocument#Site%20History.

SITE NAME: KINGS BAY NAVY SUBMARINE BASE

Contact

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Site Description

Kings Bay is a 16,000-acre facility in Camden County, Georgia that serves as the home port for the next generation of ballistic submarines support facilities for the U.S. Atlantic Fleet. Site 11 is the location of a former 25-acre landfill, known as the Old Camden County Landfill, which was operated by the county during the mid-1970s to 1980. A variety of wastes from the local community and the Navy were disposed in the landfill. Site investigations found the groundwater in the area to be contaminated with PCE, as well as TCE, DCE, and VC. In 1994, Navy Submarine Base Kings Bay entered into a Corrective Action Consent Order with the

Highlight included in Section 4.1:

Text Box 4-1. Kings Bay, Coupling Technologies

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 μ g/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 injections of emulsified vegetable oil returned the aquifer to anaerobic conditions. By 2004, VOC concentrations were reduced to <14 μ g/L, and MCLs were met at the property boundary.

Georgia Environmental Protection Division to address prior releases of hazardous constituents from Site 11, and a GETS was constructed. In 1998, the extraction system was found to not completely capture the plume, and the Navy selected ISCO using Fenton's reagent to expedite and improve the remedy rather than expand the existing treatment system. The Navy's approach was to use ISCO to reduce groundwater contaminant concentrations in the source area, followed by anaerobic biodegradation to address residual contamination, and thereby be allowed to terminate the ongoing GETS.

Objectives

A treatment objective of 100 μ g/L total chlorinated aliphatic compounds in the treatment area was selected as the functional objective for source remediation, based on the natural attenuation capacity of the aquifer (Chapelle and Bradley 1998). A reduction to this concentration was anticipated to result in degradation of all COCs to regulatory levels at the base boundary adjacent to the site.

Remedial Approach

The ISCO treatment was conducted in four phases. Each phase consisted of installation of injection wells, injection of Fenton's reagent solution, and post-treatment monitoring. Phase 1 focused on the primary source area. Phases 2 and 3 expanded the treatment area to both downgradient and upgradient areas. Comprehensive groundwater sampling after each phase was conducted to optimize the next phase. One portion of the site exhibited consistent rebound of PCE concentrations. A focused soil removal was conducted, during which crushed PCE containers and contaminated soil were removed. A fourth and final phase of Fenton's reagent injection was conducted to complete the ISCO program. Following the ISCO program, an engineered anaerobic bioremediation remedy was implemented using vegetable oil as the organic carbon substrate.

Performance

The Phase 1 injection demonstrated that Fenton's reagent ISCO could achieve the remediation goals, and Phases 2 and 3 expanded the treatment area. The comprehensive sampling program and dense network of monitoring and injection wells were critical in identifying a rebounding area at the site and ultimately for identifying the shallow DNAPL source zone that was removed by excavation. The remedial objective of 100 μ g/L total chlorinated aliphatic compounds was achieved throughout the site following the soil removal and Phase 4 of the ISCO injection. The long-term degradation of the source area following implementation of the anaerobic bioremediation treatment has been closely monitored since 2002. VOC concentrations throughout the site have remained below the 100 μ g/L goal and have continued to degrade nearly to MCLs.

Remedy Evaluation

See "Performance."

Outcomes and Challenges

The Kings Bay site has been carefully monitored by the U.S. Geological Survey for the impact on the natural attenuation capacity of the site, recovery of the microbial population, and success of an anaerobic bioremediation system at the site following the Fenton's reagent ISCO program. The most significant outcome regarding Fenton's reagent ISCO in general is that treatment does not result in sterilization of the aquifer and anaerobic microbial activity returned relatively quickly at the site. The results also demonstrated the value of very dense sampling to identify DNAPL sources; the final identification and removal of the source was probably critical in ensuring the ultimate success of the project and achievement of remedial goals. The GETS was terminated, thereby eliminating a significant expansion of the system and at least 30 years of continuing O&M.

References and Links

- Chapelle, F. H., and P. M. Bradley. 1998. "Selecting Remediation Goals by Assessing the Natural Attenuation Capacity of Ground-Water Systems," *Bioremediation Journal* **2**(3–4): 227–38.
- Chapelle, F. H., P. M. Bradley, and C. C. Casey. 2005. "Behavior of a Chlorinated Ethene Plume Following Source-Area Treatment with Fenton's Reagent," *Ground Water Monitoring and Remediation* 25(2): 131–41.
- Chapelle, F. H., M. A. Widdowson, J. S. Brauner, E. Mendez, and C. C. Casey. 2003. Methodology for Estimating Times of Remediation Associated with Monitored Natural Attenuation. U.S. Geological Survey Water-Resources Investigations Report 03-4067.
- USEPA (U.S. Environmental Protection Agency). 2004. DNAPL Remediation: Selected Projects Approaching Regulatory Closure. EPA/542/R-04/016.

SITE NAME: GOLD COAST

Contact

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Site Description

Gold Coast is a 2-acre property used to operate a mineral spirits and lacquer thinner distillation factory. Companies disposed of all spent oil and solvent waste on site, either by direct discharge to the soil or improper tank storage. The soil was heavily contaminated with heavy metals and organics, and groundwater contained VOCs at levels that exceeded drinking water standards. Twenty-five hundred corroded drums full of distillation/paint sludge and contaminated soils were found leaking into the subsurface, in addition to large hazardous waste storage tanks and a tank truck.

The groundwater at Gold Coast lies 5 feet bgs and is part of the Biscayne Aquifer that supplies drinking water to Dade County. The extensive groundwater contamination posed a significant risk to humans and the environment, and USEPA placed the site on the National Priorities List (NPL) in September 1983 (www.epa.gov/region4/waste/npl/nplfls/gldcstfl.htm#back).

The COCs at Gold Coast were VOCs, including the chlorinated solvents TCE and PCE. The following table provides a full list of COCs found at the site, initial concentrations, MCLs, ROD remediation goals, and post-treatment reductions. DNAPL was present in the groundwater, as indicated by the presence of TCE and PCE at greater than 1% and 60% of their aqueous solubilities, respectively, as well as by visual observations on site. A 0.87-acre (areally) TCE/PCE plume developed in the DNAPL source area with an estimated volume of 2,834,700 gal.

reductions (µg/L) (Sources. USELA 1998, USACE 2001.)								
СОС	2001 federal MCL	1997 ROD standard ^a	Maximum initial concentration	1991 concentration (after 1 year of	October 1996 concentration (1 year after P&T			
	value			P&T)	shut down)			
1,1-dichloroethane	None ^b	5	2,000	Below MCL	BDL^{c}			
trans-1,2-DCE	100	70	3,000	Below MCL	BDL			
Methylene chloride	5	5	100	Below MCL	BDL			
Toluene	1,000	340	545	Below MCL	BDL			
PCE	5	0.7	100,000 (avg. 176)	8	BDL			
TCE	5	3	48,000 (avg. 88)	9	BDL			

Contaminants of concern at Gold Coast Oil Superfund site: Goals, maximums, and reductions (µg/L) (*Sources*: USEPA 1998, USACE 2001.)

^{*a*} The ROD standards are at or below federal MCLs.

^{*b*} MCL for 1,1- dichloroethane is 5 μ g/L.

^{*c*} BDL = below detection limit (PCE detection limit = 0.5; for all other compounds, detection limit = 1.0)

Objectives

See table above.

Remedial Approach

The remedy included P&T followed by air sparging. After the ROD was issued in 1987, drum and tank removal and disposal occurred immediately. Removal of 683 tons of contaminated soils and hardened waste sludges occurred 1989–1990. The contaminant plume had not reached any private or municipal wells.

A P&T system operated from July 1990 to March 1994, treating extracted groundwater with an air stripper before discharging it into the Biscayne Aquifer. The groundwater recovery, treatment, and discharge system operated 21 wells and 2 air strippers. The porous limestone facilitated groundwater extraction (USEPA 1998). Within 1 year of operation, the groundwater extraction system treated over 25 million gal of water and reduced all COC concentration levels to below ROD goals with the exception of TCE and PCE. The remaining contamination was confined to two monitoring wells in the suspected DNAPL zone.

Subsequent remedial action focused on the chlorinated-solvent groundwater plume, the source of which was most likely residual DNAPL trapped in the aquifer matrix (USEPA 1998). Two unsuccessful attempts were made to address the PCE/TCE plume surrounding these wells. First, hydrogen peroxide was applied to the contaminated groundwater from March through July 1993. Second, the P&T system was shut down from August to November 1993 to encourage TCE/PCE desorption from the aquifer matrix into the groundwater. However, no significant desorption increase occurred, and dissolved TCE/PCE lingered in groundwater in this area due to low hydraulic gradient that essentially prevented groundwater movement without pumping (USEPA 1998).

Neither of these actions achieved significant reductions in contaminant concentration levels; maximum concentrations remained at $6 \mu g/L$ for TCE and $24 \mu g/L$ for PCE (USEPA 1998). The area of recalcitrant PCE/TCE was confined to a 200-square-foot area and extended to 30 feet bgs. Monitoring data during a temporary system shutdown indicated that P&T was no longer reducing concentrations, and USEPA officially shut the system down in May 1994.

In November 1994, additional soil suspected to contain DNAPL was excavated. Surprisingly, no PCE or TCE was detected in the excavated soil. Finally, the groundwater in the excavated area was sparged using a portable air sparger. Because TCE/PCE concentrations dropped below ROD goals after sparging, it appears that DNAPL was in the groundwater (saturated zone) (USEPA 1998).

Performance

Soil remediation sufficiently reduced exposure. The P&T system adequately contained the groundwater plume and even reduced its size. P&T reduced contaminant concentrations to below ROD standards except for PCE and TCE. The concentrations of PCE and TCE were significantly

reduced but stabilized, indicating the system had reached it capacity. Air sparging was used to reduce concentration of PCE and TCE to below ROD standards (USEPA 1998).

Outcomes and Challenges

Following two 5-year reviews in 1996 and 2001, the project was considered protective of human health and the environment. The Gold Coast site has been removed from the NPL.

References and Links

- USACE (U.S. Army Corps of Engineers). 2001. Superfund Five-Year Review Report, Gold Coast Oil Company, Inc., Miami, Dade County Florida. www.epa.gov/superfund/sites/fiveyear/f01-04019.pdf
- USEPA (U.S. Environmental Protection Agency). 1998. Cost and Performance Summary Report—Gold Coast Soil Superfund Site, Miami, Florida. www.frtr.gov

SITE NAME: FORMER REESE AIR FORCE BASE

Contact

None currently available.

Site Description

The former Reese Air Force Base (near Lubbock, Texas) is the site of an 18,000-foot-long dissolved-phase TCE plume covering more than 250 acres, lying in the Ogallala Aquifer, a regional alluvial fan formation that spans approximately 100–150 bgs. The Ogallala is highly heterogeneous and anisotropic, with zones of extreme high and low hydraulic conductivity interspersed throughout the affected interval. Groundwater transport velocities in the formation have been measured at greater than 5 feet/day in some areas.

Objectives

MCL for TCE, cDCE, and VC by 2014.

Remedial Approach

P&T containment.

Performance

As of 2004, the plume was contained by a 900 gpm groundwater extraction, treatment, and reinjection system that had established capture but was projected to operate for at least an additional 25 years. In 2004, the site was contracted under a guaranteed, fixed-price instrument, with the objective of restoring groundwater to MCLs or better across the entire plume footprint in 10 years.
Remedy Evaluation

The project team made several key observations that served as a basis for reworking the CSM, including the following:

- The aquifer is highly anisotropic and heterogeneous, so transport velocities will greatly exceed average groundwater velocities.
- The centerline of groundwater transport does not align directly with the groundwater elevation gradients; in the vicinity of Reese Air Force Base, there is a 40° offset between groundwater transport and the elevation grade.
- Conventional groundwater modeling and pumping strategies derived from those models will not provide optimal pumping.
- In some areas, extraction well placements may have spread contaminants laterally.

Through an iterative reconstruction of the CSM, initially using existing data from more than 700 monitoring, extraction and reinjection wells, then through additional monitoring and treatment well construction, a much different picture of the site emerged. The following are among the key findings:

- Contaminant concentration patterns are much more complex than were depicted previously with "plume limits" mapping.
- Peak TCE concentrations are notably higher than earlier recognized.
- Flow is highly organized in well-formed channel complexes that meander along the general flow axis.
- Many extraction wells were placed in locations that spread TCE laterally.

The updated site characterization data and the resulting CSM provided the basis for a substantial revision of the groundwater extraction and reinjection efforts. The CSM is continually adjusted as new data become available, and remedial system operations are adjusted quarterly, including placement of new pumping wells, as needed. With the placement of extraction points in more optimal locations and adjustment of flow allocations in response to plume behavior, the pace of plume shrinkage accelerated dramatically, and the plume area (as of March 2011) has fallen to less than 25 acres. The site is on target to reach MCLs for chlorinated VOCs, plume-wide, by 2014. The location of the extraction wells was chosen based on a fairly low-resolution mapping of contaminants. Further, the locations were often "optimized" for convenient access. In 2006 the CSM was updated to include a greater resolution regarding hydraulic flow paths, resulting in the realization that the large plume actually flowed through relatively narrow high-permeability channels conveying the majority of contaminant mass discharge. The P&T system was redesigned to focus operations on these high-flow channels, and the CSM was iteratively adjusted as new information about the site was obtained. In addition, anaerobic biostimulation was applied to the source. As a result of these improvements TCE, cDCE, and VC were all at concentrations below detection in the source area, and by 2010 the TCE plume mass had been reduced by an order of magnitude.

Outcomes and Challenges

The updated site characterization data and the resulting CSM provided the basis for a substantial revision of the groundwater extraction and reinjection efforts. The CSM is continually adjusted as new data become available and remedial system operations are adjusted quarterly, including placement of new pumping wells as needed. With the placement of extraction points in more optimal locations and adjustment of flow allocations in response to plume behavior, the pace of plume shrinkage accelerated dramatically, and the plume area (as of March 2011) has fallen to less than 25 acres. The site is on target to reach MCLs for chlorinated VOCs, plume-wide, by 2014.

SITE NAME: TEST AREA NORTH, IDAHO NATIONAL LABORATORY

Contacts

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Site Description

The Test Area North (TAN) site is of the Idaho National part Engineering and Environmental Laboratory (INEEL). Contamination at TAN included a TCE residual source area and a nearly 2-mile-long dissolved-phase plume. The plume, located within the deep, fractured basalt of the Snake River Plain aquifer, was the result of historical disposal practices at the site. including an underground injection well that was operated from the 1950s to 1972 to dispose of liquid waste streams 200-300 deep. Waste low-level streams included industrial radioactive wastewater. wastewater (including organic liquids), and sanitary sewage.

Groundwater contamination was first discovered in 1989. A thorough discussion of the complete CSM is presented in Sorenson (2000). Contaminants present in the Snake

Highlight included in Section 6.3.1:

Text Box 6-3. Test Area North, Reevaluation of the CSM

The Test Area North CSM was developed through an iterative process of identifying data gaps, conducting activities to fill those data gaps, reporting on the results of those activities, and identifying new data gaps. This process resulted in a series of four reports. Following are examples of characterization activities that have been conducted in the source area since the sludge removal activity was completed and before the ISB field test was implemented:

- Several wells have been installed within or adjacent to the source area.
- Pumping tests, slug tests, and tracer tests have been conducted to determine aquifer properties, from which residual source distribution has been inferred.
- Standard geophysical, gamma spectroscopy and acoustic televiewer logging were performed in several source area wells.
- Cross-well seismic tomography was conducted.
- Extensive groundwater sampling has been conducted throughout the source area, both in support (see Section 2.3) and prior to initiation of ISB operations.
- Furthermore, results of abiotic column studies confirmed that the dissolution of TCE DNAPL was enhanced during amendment with high concentrations of some electron donors. Of these, a whey powder solution enhanced TCE DNAPL dissolution by a factor of 6 while sodium lactate had a much smaller impact (Macbeth et al. 2006). ISB remedy was initially implemented using sodium lactate injections and then optimized with whey injections.

These activities greatly improved the understanding of aquifer hydraulic conductivity, porosity, and preferential flow paths; dissolved contaminant composition and distribution; and residual contaminant source distribution. River Plain Aquifer at the TAN site include primarily TCE, PCE, and tritium. Both cDCE and *trans*-DCE are present in the plume at low concentrations. Other contaminants of importance that appear to be associated with the sludge and are limited to the immediate vicinity of TSF-05 are cobalt (60 Co) and cesium (137 Cs).

The depth to water at TAN is approximately 200 feet. The aquifer and most of the unsaturated zone are composed primarily of layered basalt flows, intercalated with sedimentary interbeds deposited during periods of volcanic quiescence. Groundwater flow in the aquifer is controlled by the highly transmissive zones that occur during contact between individual basalt flows and, to a lesser extent, the fractured zones within flow interiors. Groundwater velocity at the site is approximately 0.4 feet/day, and porosity of the uncontaminated aquifer is 1%. Transmissivity ranges 12,000–20,000 square feet/day, with the source area being an order of magnitude less than this. The scale of the basalt geology dictates that preferential flow can be very important at spatial scales less than approximately 330 feet.

The most significant interbed is termed the "QR interbed," an apparently continuous stratigraphic unit located approximately 400 feet bgs and dipping gradually. All available data indicate this unit provides an effective bottom boundary for the contaminated aquifer.

The residual source of contamination in the aquifer is the sludge that was injected into the well more than 15-20 years ago. The pore water of the sludge probably contains large amounts of TCE, with PCE and tritium also present in significant amounts. Given the organic content of the sludge, sorbed PCE and TCE are also likely to be present. Some of the sludge has been shown to have TCE concentrations as high as 3% (by weight). The sludge, therefore, represents a longterm source of contamination to the aquifer. It has also significantly affected the properties of the aquifer in the area. The effective porosity has been estimated to be about 0.05%, which indicates that the sludge occupies much of the pore space in the source area, and the transmissivity is about an order of magnitude lower than that of nearby wells. Both gamma logs measuring radionuclides associated with the sludge and tracer tests measuring effective porosity yield an estimated radius for the sludge distribution of about 100 feet, with most of the sludge being present in the upper 100 feet of aquifer. The sludge is also very important because of the organic material available in the residual source area that creates a very different geomicrobiological environment than is present in the fringe and even in most of the core. Prior to bioremediation activities, redox conditions were mildly reducing near the injection well but were aerobic throughout most of the plume.

The distribution of TCE at TAN exemplifies the fringe-and-core hypothesis for the anatomy of chlorinated-solvent plumes (Cherry 1997). A very large, low-concentration fringe surrounds and emanates from a much smaller, high-concentration core (see figure). Within the core is a very small residual source area that continues to contaminate fresh groundwater flowing through from upgradient. A transition occurs from the scale of the residual source, where preferential flow is significant, to the scale of the fringe, where sufficient vertical communication has been present along the flow path to create a relatively well-mixed, predictable groundwater plume.

Objectives

The overall objective of the enhanced ISB field evaluation was to determine whether intrinsic biodegradation of TCE in the plume's residual source area could be enhanced through addition of an electron donor to achieve RAOs specified in the ROD amendment (DOE-ID 2001) as follows:

- Restore the contaminated aquifer groundwater by 2095 (100 years from the signature of the ROD [DOE-ID 1995]) by reducing all COCs to below MCLs and a 1 \times 10^{-4} total cumulative carcinogenic riskbased level for future residential groundwater use and, noncarcinogens, for until the cumulative hazard index is <1.
- For aboveground treatment processes in which treated effluent will be reinjected into the aquifer, reduce the concentrations of VOCs to below MCLs and a 1×10^{-5} total risk-based level.



• Implement institutional controls to protect current and future users from health risks associated with (a) ingestion or inhalation of or dermal contact with contaminants in concentrations greater than the MCLs, (b) contaminants with a $>1 \times 10^{-4}$ cumulative carcinogenic risk-based concentration, or (c) a cumulative hazard index of >1, whichever is

more restrictive. The institutional controls shall be maintained until concentrations of all COCs are below MCLs and until the cumulative carcinogenic risk–based level is $<1 \times 10^{-4}$ and, for noncarcinogens, until the cumulative hazard index is <1. Institutional controls shall include access restrictions and warning signs.

Remedial Approach

A sludge removal action was performed in 1990, during which 55 feet of sludge was removed from the 12-inch-diameter casing of well TSF-05. An interim P&T system was installed and operated from about November 1996 to November 1998, at which time it was placed in standby mode for the ISB field evaluation. A 9-month full-scale field evaluation of ISB was performed at TAN beginning in January 1999.

A ROD amendment signed in September 2001 (DOE-ID 2001) documents regulatory approval of enhanced ISB as the final remedy for the plume hot spot and MNA as the final remedy for the distal portion of the plume. The implementation of ISB in the hot spot to achieve RAOs has been divided into individual phases with specific objectives for each phase. The *In Situ Bioremediation Remedial Action Work Plan for Test Area North Final Groundwater Remediation, Operable Unit 1-07B* (DOE-ID 2002a) and supporting documents, specifically the *In Situ Bioremediation Remedial Action Groundwater Monitoring Plan for Test Area North, Operable Unit 1-07B* (INEEL 2003) and the *ISB Operations and Maintenance Plan for Test Area North, Operable Unit 1-07B* (DOE-ID 2002b), are the governing documents. The phases are described below:

- Interim Operations Phase (11/2002–10/2003): This ISB remedy officially began in November 2002 with the Interim Operations Phase. This phase included activities designed to support a better understanding of alternative electron donors, development of injection strategies to support the Initial Operations Phase, ISB model refinement, continued ISB sodium lactate addition, and construction of the ISB facility. The results and details of activities conducted during the Interim Operations Phase are reported in the Annual Performance Report for In Situ Bioremediation Operations November 2002 to October 2003, Test Area North Operable Unit 1-07B (Armstrong et al. 2004).
- Initial Operations Phase (10/2003–current): The completion of the ISB facility marked the start of the Initial Operations Phase. The goal of this phase is to reduce VOC concentrations in downgradient wells TAN-28 and TAN-30A to below MCLs. The Initial Operations Phase will be complete when it is determined that downgradient flux from the hot spot has been reduced such that VOC concentrations remain less than MCLs at TAN-28 and TAN 30A for a period of 1 year. Activities conducted during this phase include injections into newly installed injection well TAN-1859 and initiation of a pilot test to evaluate the effectiveness of whey powder in March 2004.
- Optimization Operations Phase (future)—This phase will focus on reducing the flux of VOCs from the hot spot in the crossgradient direction, as measured at TAN-1860 and TAN-1861 while maintaining VOC flux reduction in the downgradient direction. During this

phase, data will continue to be gathered and analyzed relating to achievement of long-term performance objectives.

• Long-Term Operations Phase (future)—This phase will focus on achievement of hot spot source degradation, while maintaining the reduction of VOC flux from the hot spot in the crossgradient and downgradient directions.

Performance

The TAN monitoring well network included 17 sampling locations from 14 monitoring wells. Well TSF-05 has been used as the electron donor injection well since the beginning of the project and is sampled at two discrete depths. Well TAN-37 is sampled at three discrete depths. Sampling was performed biweekly during the field evaluation and monthly since then. The program includes parameters to monitor electron donor and nutrient distribution, redox-sensitive parameters, VOC contaminants and degradation products, biological activity indicators, and water quality parameters.

Remedy Evaluation

Periodic injection of high-concentration sodium lactate solution approximately from the water table (210 feet) to 300 feet bgs into TSF-05 was conducted during an enhanced ISB field pilot study at TAN in 1999. Groundwater samples were collected to assess redox conditions, bioactivity, and reductive dechlorination. Data collected within the residual source area during the field pilot study demonstrated that sodium lactate injections stimulated complete biological conversion of all aqueous-phase TCE to ethene within 1 year (Song et al. 2002). The stable carbon isotope data collected by Song et al. (2002) also showed that the isotope ratio of the TCE changed over time, suggesting that the nature of the source term was impacted. Since then, data collected over the course of ISB operations show significant production of ethene, indicating complete dechlorination of aqueous-phase TCE.

During the field evaluation, increases in total molar concentrations of VOCs at well locations impacted by the electron donor injections suggested that enhanced mass transfer of TCE from the residual source was occurring as a direct result of the injections. For instance, total chloroethenes in TAN-26, a deep well sampled at 389 feet bgs and approximately 50 feet downgradient from the injection well TSF-05, increased over an order of magnitude in molar concentration during injection of 30% and 60% sodium lactate. At least three potential mechanisms could have contributed to this observation:

- physical displacement of the TCE from the residual source
- desorption of TCE from the residual source
- the electron donor solution itself interacting with the residual source to enhance the dissolution and/or increase effective solubility

The first mechanism was ruled out because, while TCE concentrations increased dramatically in TAN-26, the aqueous inorganic components of the sludge, most notably tritium, did not. At the time this work was performed, the potential importance of the second and third mechanisms was

not suspected. It was proposed that the mass transfer of TCE within the residual source to the aqueous phase was somehow being preferentially enhanced by the injected sodium lactate.

Subsequent interfacial tension (IFT) measurements between TCE DNAPL and different concentrations of sodium lactate suggested that the sodium lactate might be acting as a mild surfactant or cosolvent by lowering IFT between the residual TCE and the surrounding groundwater (Sorenson 2002). In addition, this newly mobilized TCE was efficiently biodegraded.

The use of high-concentration electron donor solutions to enhance mass transfer of contaminants into the aqueous phase to facilitate rapid reductive dechlorination and residual source depletion is referred to as Bioavailability Enhancement Technology (B.E.T.[™], U.S. Patent 6,783,678). At TAN, the use of B.E.T. was critical for demonstration that enhanced ISB was a viable option for remediation of the chlorinated-solvent residual source area because accelerated mass transfer of contaminants from the residual phase to the aqueous phase makes the contaminants available for biological degradation and significantly shortens the overall remedial time frame.

Since the field evaluation, enhanced ISB operations over the last 6 years have resulted in the continued degradation of contaminants within the residual source area impacted by electron donor injections, as evidenced by ethene accumulation. The kinetics of the degradation reactions are such that liberated contaminants are generally observed as elevated concentrations of ethene, as opposed to TCE, cDCE, and VC concentrations, following injection events. Therefore, residual source degradation at TAN appears to be limited not by the kinetics of the degradation reactions but by the dissolution of TCE from the residual phase into the aqueous phase. Thus, optimization activities at TAN have been focused on enhancing mass transfer of VOCs to the aqueous phase to maximize degradation of the residual source, as well as reducing operation and monitoring costs and accomplishing site remediation goals. These activities have included laboratory and field tests to evaluate alternative electron donors that might be more effective than sodium lactate for ISB within a residual source area.

Laboratory studies were performed to assess several important properties of electron donors used for ISB, including effectiveness in stimulating degradation reactions, longevity or utilization rate of the electron donor, the ability to distribute electron donor over a large area through a single injection location, and ability to enhance the mass transfer of TCE DNAPL (Macbeth et al.

2006). The laboratory studies included IFT analyses of different concentrations of the electron donor solutions, microcosm studies using a TCE-dechlorinating culture molecular enriched from groundwater. TAN of the microbial characterization communities stimulated by the various electron donors, and column studies to evaluate the abiotic enhanced dissolution effect of high and low concentrations of the electron donors on TCE DNAPL. The results of the abiotic column studies confirmed that the dissolution of TCE DNAPL was enhanced during amendment with high concentrations of some electron donors. Of these, a

Highlight included in Section 6.2.1:

Text Box 6-2. Test Area North, Optimizing In Situ Treatment

The results of abiotic column studies confirmed that the dissolution of TCE DNAPL was enhanced during amendment with high concentrations of some electron donors. Of these, a whey powder solution enhanced TCE DNAPL dissolution by a factor of 6 while sodium lactate had a much smaller impact (Macbeth et al. 2006). whey powder solution enhanced TCE DNAPL dissolution by a factor of 6 over that observed during potable water amendment, while sodium lactate had a much smaller impact (Macbeth et al. 2006).

Based on the collective results of the laboratory studies, a field-scale pilot test was conducted to examine the extent of enhanced mass transfer and subsequent dechlorination of TCE from the residual source area at TAN in response to injections of whey powder as compared to sodium lactate. The pilot test was implemented in two phases, the first of which involved high-resolution monitoring following two injections of sodium lactate conducted in March and May of 2004.

Following these injections, spikes in TCE and cDCE concentrations from a baseline near 0 μ g/L up to 300–400 μ g/L at the injection well and up to 25–75 μ g/L 25 feet downgradient were observed. In addition, there were dramatic increases in ethene concentrations within 48 hours, indicating rapid dechlorination of the newly bioavailable TCE.

Phase 2 of the pilot test involved three cycles of whey powder injections conducted in August and October 2004 and January 2005. These injections resulted in spikes in TCE and cDCE concentrations from near 0 μ g/L up to 400–600 μ g/L within the injection well and up to 250– 400 μ g/L 25 feet downgradient. In addition, the total chloroethene and ethene molar areas were evaluated during these injection cycles to compare the total mass of contaminants liberated and subsequently degraded to ethene. The total molar areas were approximately three times greater during a whey injection cycle compared to sodium lactate. The rate at which the molar area increased (indicator for mass removal rate) was calculated to be 50%–250% higher during a whey powder injection cycle than for sodium lactate. These data indicate that whey powder enhanced mass transfer and degradation of TCE to a greater degree than sodium lactate. The use of whey powder for long-term ISB operations is expected to increase the rate of contaminant source depletion, ultimately resulting in a reduction of the remediation time frame at TAN.

Outcomes and Challenges

The CSM for TAN was developed through an iterative process of identifying data gaps, conducting activities to fill those data gaps, reporting on the results of those activities, and identifying new data gaps. This process has resulted in a series of four reports, the last of which was Wymore, Bukowski, and Sorenson (2000). Examples of characterization activities that have been conducted in the source area since the sludge removal activity was completed and before the ISB field test was implemented are as follows:

- Several wells have been installed within or adjacent to the source area.
- Pumping tests, slug tests, and tracer tests have been conducted to determine aquifer properties, from which residual source distribution has been inferred.
- Standard geophysical, gamma spectroscopy, and acoustic televiewer logging were performed in several source area wells.
- Cross-well seismic tomography was conducted.
- Extensive groundwater sampling has been conducted throughout the source area, both in support of ISB operations (see Section 2.3) and prior to initiation of ISB activities.

These activities greatly improved the understanding of aquifer hydraulic conductivity, porosity, and preferential flow paths; dissolved contaminant composition and distribution; and residual contaminant source distribution. A thorough discussion of the complete SCM is presented in Sorenson (2000).

The TAN ISB monitoring program maximizes cost-effectiveness by using a combination of fixed laboratory and field analyses.

The source area bioremediation at TAN remains one of the largest-scale projects in a source area of its kind in the world, certainly in deep, fractured rock. An area approximately 60 m (200 feet) in diameter is being treated, initially across an aquifer thickness of 60 m (200 feet). As contaminants have been removed in the deepest part of the contaminated aquifer, which presumably was limited to aqueous- (and possibly some sorbed-)phase contamination, the focus is now on the upper 30 m (100 feet) of the aquifer. Both field and laboratory data have demonstrated that bioremediation through injection of high-concentration electron donor solutions has enhanced depletion of the residual source by enhancing mass transfer into the aqueous phase. The biodegradation kinetics have largely remained faster than the mass transfer kinetics, leading to an optimization strategy largely devoted to accelerating mass transfer rates even further. This requires continued injections of high-concentration electron donors throughout the area impacted by residual source material. As the volume of this area is large and the transmissivity of the aquifer is very high, injection volumes are larger than at many other chlorinated-solvent sites.

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SITE NAME: AIR FORCE PLANT 44, TUCSON, ARIZONA

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Site Description

Air Force Plant 44 is part of the Tucson International Airport Area (TIAA) located 8 miles south of downtown Tucson. It is bounded to the north and east by the Tucson International Airport, to the South by Hughes Access Road, and to the West by the Nogales Highway Route 89. The facility is part of the TIAA CERCLA site.

The regional aquifer is composed of unconsolidated to semiconsolidated basin-fill alluvium divided into upper and lower zones. The upper zone is 90–140 feet bgs, more permeable than the lower zone, and the focus on most of the remediation efforts. Groundwater flows northwesterly in the southern part of the well field and almost due north in the northern part of the well field. The change in flow direction is controlled by variation in the stratigraphy of the subsurface and controls the areal shape of the plume. The treatment site covers of the southern half of a 6-mile-long TIAA TCE plume.



Air Force Plant 44 (AEP-44) Raytheon Project Area. Source: www.azdeq.gov/environ/waste/sps/download/tucson/rayt heon.pdf.

Highlight included in Section 5.5.2:

Text Box 5-2. Air Force Plant 44, Stable Trend Resulting in a Change in the Remedy

TCE values immediately below the former disposal areas indicated that mass discharge equaled mass removed using the P&T system. This finding resulted in the decision to remove the source areas while still operating the P&T system.

Objectives

Drinking water quality in the regional aquifer.

Remedial Approach

In 1987 P&T was installed to treat the southern half of the 6-mile-long TIAA Superfund site using a 2-square-mile well field including 15 extraction wells located in the middle and at the downgradient end of the plume and 16 discharge wells located along the plume margins to enhance flushing and containment (Allen, Katz, and Warner 2005). The treatment plant design capacity was 4500 gpm using air stripping. In the early 1990s the P&T system successfully contained the TCE plume and eliminated almost all chromium in the downgradient potion of the plume but was ineffective near the former solvent-disposal locations. These proved to be ongoing sources of TCE. Fine-grained sediments in the uppermost part of the regional aquifer and immediately downgradient of the source areas continued to have the highest TCE concentrations. Soil gas samples identified high VOC in the unsaturated zone above the former disposal areas. TCE values immediately below the former disposal areas indicated that mass discharge equaled mass removed using the P&T system. This resulted in the decision to remove the source areas while still operating the P&T system.

SVE and dual-phase extraction were installed at all former solvent disposal areas in the early 1990s, and by 1999 the first disposal area was remediated and closed. The second was near performance standards, and two others were making significant progress. Regardless, TCE concentrations in groundwater beneath these former disposal areas displayed little improvement. Full-scale application of potassium permanganate began in 2003 on a 15-acre site using 15,000 pounds of potassium permanganate in 0.5% solution injected into the upper part of the aquifer using former monitoring and extraction wells. Six thousand pounds of potassium permanganate at 0.3% solution was injected through former SVE wells into the lower aquifer. Pumping was started in 2004 to improve potassium permanganate distribution.

Concentrations declined from an average of 297 μ g/L in 2001 to 28 μ g/L in February 2005 (90% reduction). Rebound has occurred, requiring additional injections.

Performance

This remedial approach has prevented ongoing migration of the plume further into sole source drinking water aquifer, quickly reducing risk/exposures for local residents; DNAPL source removals have shrunk plume dimensions such that the pumping rate achieves adequate capture with 50% of the original flow rate; SVE in DNAPL source zones has resulted in site closure and significant reduction in groundwater concentrations; ISCO in saturated DNAPL source zones has reduced mass flux, helping the U.S. Air Force argue for a revised containment strategy that will further reduce flow rates and associated costs. Initial P&T, enhanced by DNAPL source zone remediation, has reduced mass flux overall by 97.8%.

Remedy Evaluation

A new CSM indicated that even though the SVE had effectively removed TCE from the vadose zone, chlorinated-solvent contamination was still discharging to the downgradient aquifer due to diffuse storage in fine-grained materials in the capillary fringe and in the upper part of the aquifer material. SVE could not effectively remove this material. To remove this diffuse storage contamination ISCO using potassium permanganate was tested and applied.

Outcomes and Challenges

Highlight included in Section 2.3:

Text Box 2-1. Air Force Plant 44, Diffusive Storage

A new CSM indicated that even though SVE had effectively removed TCE from the vadose zone, chlorinated-solvent contamination was still discharging to the downgradient aquifer due to diffuse storage in fine-grained materials in the capillary fringe and in the upper part of the aquifer material. SVE did not effectively remove this material.

Agencies are recommending further DNAPL source area actions, which the U.S. Air Force does not agree are necessary.

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SITE NAME: CALDWELL TRUCKING, FAIRFIELD TOWNSHIP, NEW JERSEY

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Site Description

The Caldwell Trucking site is an 11.25-acre facility that hauled and stored sewage from the early 1950s through 1988. Disposed of industrial waste and residential/commercial septic waste in unlined lagoons caused contamination on site. In 1973 underground storage tanks were used to hold waste before off-site

Highlight included in Section 6.2.1:

Text Box 6-1. Caldwell Trucking, Optimizing In Situ Treatment

A full-scale field test using enhanced biological treatment from January 2001 to July 2002 was designed to determine whether enhanced bioremediation was viable to treat residual DNAPL in the basalt bedrock. The test goals were to accelerate the dissolution and treatment of source material and reduce the overall lifetime and impact of the source, rather than to achieve specific concentration reductions (NRC 2005).

disposal. Waste storage was abandoned in the early 1980s. In 1988, all operations ended.

The source of soil, sludge, and groundwater contamination is industrial waste that was discharged into unlined lagoons from the 1950s through the early 1970s. A CVOC groundwater plume extends 4000 feet downgradient of the lagoons in the direction of the Passaic River (USEPA 2007).

The primary COCs in groundwater at the site and nearby surface waters (e.g., the Passaic River) are CVOCs (e.g., PCE, TCE, and daughter products). Residual DNAPL is suspected in a fractured basalt bedrock aquifer beneath a glacial sand and gravel aquifer. TCE was detected in this source zone at levels up to 700 mg/L in 2005. The soil contains metals, VOCs, SVOCs (polycyclic aromatic hydrocarbons [PAHs]), and polychlorinated biphenyls, largely from underground storage tanks (NRC 2005).

Since 1981 over 300 private drinking wells have been closed due to VOC groundwater contamination off site. The 1986 Operable Unit (OU)-1 ROD required excavation of contaminated soil, air stripping a municipal water supply well, and an alternative water supply for off-site residents. Air-stripping was subsequently removed since a decision was made not to use the well. The soil remedy was adjusted to address disposal of certain waste materials and stabilization of lead-contaminated soils. In 1995 excavation and off-site disposal of soils with VOC concentrations >100 mg/kg and in situ S/S of remaining soil contamination was added. An SVE system was also installed to minimize odors and soil gas emissions during S/S.

In 1989 P&T was required to intercept the groundwater plume, plus a technical impracticability waiver for groundwater was prepared. USEPA was unable to install groundwater recovery wells in 15 locations due to access conflicts with local property owners, so wells were installed in the most highly contaminated areas of the lower water table aquifer and the upper bedrock aquifer (USEPA 2007).

Objectives

The principal responsible parties amended the P&T remedy to be replaced with enhanced ISB (EISB). The EISB system continues to perform voluntary bioaugmentation of the source zone. The 2007 5-year review indicated that groundwater contamination concentration levels are steadily decreasing but remain above MCLs.

Remedial Approach

Remedial action included removal of underground storage tanks, excavation of soil and waste material, S/S of metal-contaminated soils, SVE of VOCs in the unsaturated zone, installation of an iron reactive barrier wall with a supplemental seep remediation system, EISB, and hydraulic containment using P&T.

The SVE system operated from June 1996 to March 1997, when it was shut down due to odor complaints (NRC 2005). Next, 40,000 cubic yards of contaminated soils was stabilized from March through September of 1997. Additionally, an iron reactive wall was installed to intercept contaminated groundwater as it flows towards a surface water seep. The anticipated abiotic

degradation as groundwater passed through the reactive wall did not sufficiently reduce contaminant concentrations to target levels, so an air stripper was installed to replace the reactive wall treatment.

A full-scale field test was conducted using enhanced biological treatment from January 2001 to July 2002. The test was designed to determine whether enhanced bioremediation was viable to treat residual DNAPL in the basalt bedrock, which is the source of the VOC plume. The test goals were to accelerate the dissolution and treatment of source material and reduce the overall lifetime and impact of the source rather than to achieve specific concentration reductions (NRC 2005).

Ambient groundwater conditions at the site appear to support natural degradation of TCE at low levels. A substrate feed of lactate, methanol, and ethanol and a microbial supplement of *Dehalococcoides ethenogenes* were injected into six nutrient injection wells screened in glacial deposits and bedrock. Seven monitoring wells were also installed.

A vapor intrusion study included approximately 120 additional properties. Sampling began at residential and commercial properties downgradient of the site in April 2007. Mitigation systems have been installed and up to 25 systems may be required (Ryan 2010).

Performance

The SVE system recovered over 25,000 pounds of VOCs from the soil in 1 year (USEPA 2005). The EISB field test induced bacterial reductive dechlorination of contaminants in the residual DNAPL source zone during its 18-month test through July 2002. During a 30-month monitoring period, net reductions in PCE and TCE concentrations averaged 95% and 93%, respectively (see table) across the treatment zone (NRC 2005).

Location	Compound	Initial concentration (µg/L)	Concentration reduction (µg/L)	Average net reduction in concentration (%)	Degradation product production (µg/L)
Entire	TCE	700,000	790	93	Average observed ethene
treatment zone	PCE	No results	131	94	concentration was 723.
Well C-22	TCE	680,000	1,700	99.8	cDCE went from nondetect to
(highest initial	PCE	27,000	260	99.0	36,000 (then declined to
concentrations)					27,000); VC sustained at 2,000;
					ethene sustained at 30-40.

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Sources: Finn et al. 2003, NRC 2005, USEPA 2010.

Two of seven monitoring wells in the EISB treatment area contained no PCE after the 30 months, and one well had no detectable TCE. Breakdown products such as DCE and VC remained at elevated concentrations in several wells (NRC 2005), including the following:

• MW-B23: This overburden monitoring well exhibited disappearance of PCE and TCE coupled with ethene production. Concentrations of cDCE remained elevated, and VC

increased from December 2000 to December 2002. From December 2002 to September 2003, concentrations of both cDCE and VC decreased to less than 20 μ moles/L.

- MW-C22: This bedrock monitoring well had the highest TCE and PCE concentrations prior to EISB treatment. Post-treatment samples detected mixture of cDCE, VC, and ethene.
- Significant solvent reductions occurred in both injection wells and monitoring wells, accompanied by large increases in ethene concentrations, indicating that a continuous treatment zone was present across the test area (NRC 2005).

Remedy Evaluation

The principal responsible parties have amended the EISB system and continue to perform voluntary bioaugmentation of the source zone. The 2007 5-year review indicated that groundwater contamination concentration levels are steadily decreasing but remain above MCLs. Remedial activities continue and optimization studies are under way (USEPA 2007).

With the excavation and off-site disposal of contaminated material and stabilization of the remaining contaminated soil and waste materials at the site, all on-site soil contamination has now been removed or rendered harmless. The restored wetlands monitoring is complete after 5 years. The use of an alternative drinking water supply by affected homes and businesses in the area of the Caldwell Trucking site has significantly reduced the potential for exposure to contaminated groundwater. However, high levels of groundwater contamination still remain, and the principal responsible parties have completed the construction of a P&T containment facility to remediate the contaminated groundwater near the source area using extraction wells in the vicinity of O'Connor Drive. The upgrade of the seep area treatment system has been completed, and additional investigations are being conducted. A vapor intrusion study is also nearing completion (USEPA 2010).

Outcomes and Challenges

The principal responsible parties wanted to amend the P&T remedy and replace it with EISB. USEPA has not approved the amendment since EISB does appear to be reducing VOC levels in the source zone and daughter products remain at elevated concentrations, indicating that P&T is necessary to hydraulically contain the groundwater plume (USEPA 2007). A P&T system was installed in December 2008. Monitoring data to date indicate that it is functioning as intended and that the most highly contaminated portion of the plume is contained (Ryan 2010).

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SITE NAME: FORT LEWIS—EAST GATE DISPOSAL YARD

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Site Description

The East Gate Disposal Yard (EGDY) at is the source of a large TCE plume at the Logistics Center Site in Fort Lewis, Washington. The EGDY was used between 1946 and the 1970s as a disposal site for waste generated at the Logistics Center. While petroleum, oils, lubricants, PCE, TCE and its

Highlight included in Section 5.1:

Text Box 5-1. Fort Lewis East Gate Disposal Yard, Strategic Monitoring

The Fort Lewis East Gate Disposal Yard remedial action is a prime example case study showing how strategic monitoring resulted in more effective and efficient cleanup of chlorinated solvents. In 1998 an Explanation of Significant Difference was issued to allow further investigation into the nature and extent of the COCs as well as to enhance the selected remedy. This understanding allowed innovative treatment strategies to be considered, such as the Triad approach for characterizing migration of COCs, as well as the use of ERH to remove the NAPL. Having this flexibility in place was instrumental in the practitioners' ability to make modifications during all phases of remedial action, from initial installation to relocating to the additional areas needing treatment, to ensure remedial process performance.

degradation products cDCE and VC were all detected at EGDY, TCE is the primary COC. TCE is present in multiple locations over the 23-acre source area, often as a NAPL. The most highly contaminated areas have been designated as NAPL Areas 1, 2, and 3.

The TCE plume extends down the Vashon Aquifer from the source area for approximately 2 miles. About halfway down this plume, TCE also enters the Sea-Level Aquifer (SLA) via a hydrogeologic preferential pathway, from which it extends in the SLA for approximately 2.5 miles. The level of TCE in both aquifers exceeds the ROD goal of 5 μ g/L, which is the drinking water standard for TCE. TCE has been historically detected in the groundwater beneath the Logistics Center at a maximum concentration of 100,000 μ g/L (USEPA 2007).

Objectives

Restore groundwater to MCLs and prevent contamination above MCLs from spreading beyond the site boundaries (Ryan 2010, USEPA 2010).

Remedial Approach

In 1985 groundwater contaminated with TCE was confirmed. P&T was selected as the preferred remedy for the upper aquifer and also for the lower aquifer as necessary. The P&T system for the upper aquifer began operations in 1995. The source area investigation began in 1999 and was completed in 2002 with an engineering evaluation/cost analysis and drum removal remedial activity occurring between two investigation phases (USEPA 2005).

Performance

ERH has effectively targeted NAPL source zones at EGDY. Performance results indicate that 12,787 pounds of VOCs has been extracted, groundwater TCE concentrations have reduced from 100 ppm to <100 ppb, soil TCE concentrations have been reduced by 96%, and contaminant mass flux has reduced by 60%–90% (Ryan 2010). According to a 2009 assessment of ERH at EGDY, "ERH treatment appeared to be robust in removing mass from the targeted zone with a minimal rebound of contamination observed" (Truex et al. 2009). The thermal remediation project at the Logistics Center was successful and can be used a model for future thermal operations.

Remedy Evaluation

The EGDY remedial action is a prime example case study showing how strategic monitoring resulted in more effective and efficient cleanup of chlorinated solvents. In 1998 an Explanation of Significant Difference was issued to allow further investigation into the nature and extent of the COCs as well as to enhance the selected remedy. This understanding allowed innovative treatment strategies to be considered, such as the Triad approach for characterizing migration of COCs as well as the use of ERH to remove the NAPL. Having this flexibility in place was instrumental in the practitioner's ability to make modifications during all phases of remedial action, from initial installation to relocating to the additional areas needing treatment, to ensure remedial process performance. One instance of the success of this flexibility occurred during the initial remedial action at Area 1, when operational data indicated that the original contracted temperature requirements for NAPL removal would not be achieved throughout each of the areas being treated. Using accumulated data gathered during subsequent drilling activities associated with implementation of the ERH installation, the practitioner was able to modify the temperature specification at areas of known NAPL concentrations or areas indicating a high probability of having NAPL. As the ERH operations progressed, real-time data collection (vapor and groundwater) was used to continually modify the ERH application to address possible or potential areas where NAPL may be present. The lessons learned in the adaptation of the ERH application in Area 1 were incorporated into Areas 2 and resulted in shorter operational time frames to achieve successful removal of NAPL.

Outcomes and Challenges

The innovated use of treatment technologies and strategies for this chlorinated-solvent site resulted in the average concentrations of TCE dropping from a historical maximum of 100 ppm to below 100 ppb, with future land uses identified as commercial or industrial and future land uses downgradient of the source zone primarily industrial with some residential and open space. Because of this successful outcome implementing an innovated thermal treatment technology, the Fort Lewis site received the 2005 Secretary of Defense Environmental Award for Environmental Restoration.

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SITE NAME: LAUNCH COMPLEX 34

Contact

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Site Description

Hydrogeological conditions at Launch Complex (LC)-34 are highly favorable to the implementation of a recirculationbased remediation technology. The aquifer consists of relatively homogeneous sand and silty sands and is easily instrumented using low-cost, direct-push drilling technologies (e.g., GeoProbe). A surficial aquifer and a semiconfined aquifer beneath a clay unit compose the major waterbearing units at LC-34. The surficial aquifer extends from the water table to

Highlight included in Section 4.2:

Text Box 4-4. Launch Complex 34, Sequential Treatment Compared to Individual Technologies

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-footlong, 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 bos. 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.

approximately 45 feet bgs. The clay confining unit ranges in thickness 1–3 feet. The surficial aquifer is subdivided into the upper sand unit (USU), the middle fine-grained unit (MFGU), and the lower sand unit (LSU) (Eddy-Dilek et al. 1998). The USU is composed of medium- to coarse-grained sand and crushed shells and extends from ground surface to approximately 18–25 feet bgs. The MFGU, which varies in thickness about 4–14 feet, is composed of gray, fine-grained silty/clayey sand and generally contains finer-grained sediment than the remainder of the aquifer unit. The MFGU is thicker to the north of the Engineering Support Building (ESB) and appears to thin towards the south and west of the ESB. The LSU, the deepest subunit of the surficial aquifer, consists of gray fine to medium-sized sand and shell fragments. In addition, the LSU contains some isolated fine-grained lenses of silt and/or clay. The thickness of the clay unit to prevent drilling-induced migration from the LSU into the confined aquifer. The confining unit may act as a barrier to DNAPL migration into the confined aquifer.

The Atlantic Ocean is located immediately to the east of LC-34. To determine the effects of tidal influences on the groundwater system, water levels were monitored in 12 piezometers over a 50-hour period during RCRA facility investigation activities (G&E Engineering, Inc. 1996). All the piezometers used in the study were screened in the surficial aquifer. No detectable effects from the tidal cycles were identified in the subject area. However, the Atlantic Ocean and the Banana River (west of LC-34) are sufficiently close to the site and appear to act as hydraulic barriers or sinks, as groundwater likely flows toward these surface water bodies and discharges into them. Other hydrologic influences at LC-34 include features such as paving, constructed drainage ditches, and topographical relief. Permeable soils exist from the ground surface to the

water table, and drainage is excellent. Water infiltrates directly to the water table. Only limited data were available to characterize background geochemistry at LC-34 (Battelle 1999) prior to the sequential technology demonstration. As may be expected, the salinity of groundwater in the surficial units increases with depth with concentrations of total dissolved solids as high as 1200 mg/L in the LSU (predominantly Na, K, Mg, Ca, Al, Cl, and total SO₄/S). Groundwater pH is near neutral (7.3–8.0) with an alkalinity of up to 360 mg/L (as CaCO₃). Although no direct measurements of redox potential are available, the high concentrations of dissolved iron and manganese indicate that the groundwater redox potential is generally reducing.

A preliminary site investigation was conducted by Geosyntec in December 2002 to facilitate selection of locations for the ISCO pilot demonstration. Five boreholes were drilled within the ISCO pilot test area adjacent to the ESB to characterize the geology and the soil and groundwater chemistry. Soil samples from five boreholes were submitted for laboratory analysis of VOCs. The presence of DNAPL was inferred based on photoionization detector readings exceeding 9,999 ppm by volume and concentrations of TCE in soil exceeding 10,800 mg/kg. Appendix A of the Project ER-0116 final report provides a detailed summary of the preliminary site investigation.

Objectives

The main objectives of this project were to assess the technical feasibility of sequential application of these technologies and to identify the optimal timing of the transition from ISCO to ISB. The principal benefit of ISCO using permanganate (MnO_4^-) is that it aggressively enhances dissolution and destruction of the target contaminants within a relatively short period of time (i.e., months to years); however, the cost-benefit of this technology diminishes as the mass of target chemicals decreases. The most effective application of ISCO consists of rapid destruction of the readily accessible target chemical mass within the source area although it can also be coupled with a less costly in situ remediation mass removal technology such as ISB.

Remedial Approach

Sequential application of ISCO and ISB is potentially widely applicable at chlorinated-solvent sites throughout North America. However, several issues may potentially limit the widespread application of this technology. In the long term, ISCO application using permanganate is likely to increase the concentration of manganese in soil and groundwater, a potentially adverse geochemical impact with respect to subsequent treatment by ISB. The cost and performance of ISB, both using biostimulation and bioaugmentation, were evaluated at the LC-34 technology demonstration site. A number of remediation technology demonstrations for treatment of DNAPL dominated by TCE have been conducted at LC-34, including ISCO using permanganate (completed 2000), six-phase heating (completed 2001), and steam flushing (completed 2002). In addition, smaller-scale demonstrations of ISB using bioaugmentation and emulsified ZVI were also conducted.

Implementing two source-control technologies (ISCO and ISB) may add cost and performance barriers to implementation. However, implementing these technologies sequentially may provide substantial schedule and performance advantages when implemented in a compatible manner, off-setting the increased capital costs with reduced O&M costs. The uncertainty surrounding the performance of these coupled technologies is another barrier, particularly at full scale.

Prior to this project, little had been documented regarding the field-scale impact of ISCO on groundwater geochemistry and microbiology of TCE DNAPL treatment by ISB. Specifically, the application of an aggressive dose of permanganate may have adverse impacts on the indigenous microbial community and the cost of post-ISCO ISB. A field trial evaluating biostimulation and/or bioaugmentation after aggressive permanganate treatment at LC-34 was conducted. Specifically, ISB was evaluated with respect to the completeness of dechlorination and the effect on mass flux emanating from a source zone.

During the demonstration, groundwater was recirculated through the ISCO-treated area at a constant groundwater velocity. A number of treatment phases were used to evaluate the rate of DNAPL removal and the extent of VOC treatment. Each phase was operated under each of the different operating conditions (i.e., baseline groundwater recirculation only, electron donor addition, electron donor addition, plus bioaugmentation).

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 dimensions of 100 feet long by 100 feet wide source area with 12,500 pounds of TCE (sum of TCE as DNAPL, on soil and at approximately175 mg/L in groundwater) present from 10 to 80 feet. The geology was assumed to be composed of a sand unit from 10 to 40 feet and a silty sand unit from 40 to 80 feet. 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.

Sequential application of ISCO and ISB is potentially widely applicable at chlorinated-solvent sites throughout North America. However, several issues may potentially limit the widespread application of this technology. In the long term, ISCO application is likely to increase the concentration of manganese in groundwater, a potentially adverse geochemical impact. The capital cost associated with implementing two source-control technologies (ISCO and ISB) may be a barrier to implementation. However, implementing these technologies sequentially may provide substantial schedule advantages over the implementation of either technology alone, off-setting the increased capital costs with reduced O&M costs.

Performance

The principal results of the project include the following:

- Electron donor addition (ISB) after ISCO resulted in partial biodegradation of TCE, with complete biodegradation observed after bioaugmentation.
- At the field-scale, ISB did not increase the mass flux of chloroethenes after ISCO.
- The precipitated manganese dioxide produced by MnO₄ reduction, which can oxidize some organic compounds, did not abiotically degrade any of the chloroethenes or ethene.

- Manganese dioxide (MnO₂) greatly increases the electron donor demand above that typically required to reduced the dissolved constituents (e.g., oxygen, nitrate, sulfate, and the target chloroethenes) during ISB.
- MnO₂ can be dissolved by the activity of Mn(IV)-reducing bacteria, which appear to preferentially use hydrogen and inhibit the activity of dechlorinating microorganisms (i.e., *Dehalococcoides*, which use hydrogen as their sole electron donor).
- The limited cost assessment indicated that there was a significant cost and schedule advantage for the sequential treatment strategy over using P&T or ISCO alone.

Remedy Evaluation

Following the ISCO demonstration at LC-34, the residual permanganate remaining in the test plot likely continued to slowly react with soil and/or residual TCE present in the subsurface while slowly migrating downgradient of the test plot. Permanganate was not observed during a groundwater monitoring event (October 2002) conducted using monitoring wells located in and adjacent to the test plot, suggesting that the residual permanganate was depleted, which was an essential step prior to initiating treatment via bioremediation.

Pre- and post-treatment soil sampling was performed by Battelle during the previous technology demonstrations (Battelle 2001). The results of post-treatment monitoring in the ISCO test plot indicate that 844 kg of total TCE mass, including 637 kg of TCE DNAPL, remained in the LSU.

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SITE NAME: PALL AEROPOWER

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Site Description

Six chlorinated-solvent source areas beneath the former Pall Aeropower facility in Tampa, Florida

Highlight included in Section 4.1.3.1:

Text Box 4-2. Pall Aeropower, Rebound from Desorption

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 soiladsorbed CVOCs caused contaminant concentrations to rebound after the oxidants were consumed.

support five plumes up to 600 feet long. Chloroethene solvents were used at the site 1972–1998. Pretreatment sampling detected TCE concentrations as high as 470,000 μ g/L and PCE concentrations as high as 110,000 μ g/L, confirming a DNAPL phase was present. Based on compound solubilities, DNAPL was suspected at two locations. cDCE and VC, which are daughter compounds of PCE and TCE, and eight other VOCs also are present.

Site soils are fine sand to a depth of ~15 feet. Silty fine sand extends 15–28 feet bgs; the majority of CVOCs were found in the deeper interval. Two to three feet of clayey sand or sandy clay begin at ~28 feet bgs. Silts and clays containing decomposed limestone and shell fragments are present ~30–90 feet bgs soils. CVOCs are rarely found at or below 70 feet bgs.

The water table aquifer is encountered at 3–4 feet bgs, depending on the season. Groundwater moves slowly to very slowly, approximately 8 feet/year 3–15 feet bgs, 1 foot/year 15–28 feet bgs, and <1–10 feet/year 30–90 feet bgs per year. Natural groundwater pH ranges 5.0–6.0. Natural dissolved levels of oxygen, Eh, nitrate, phosphorus, total alkalinity, and dissolved organic matter are low. Groundwater temperatures average 75°F.

Objectives

Source removal to remediate CVOCs and VOCs in groundwater in the surficial aquifer system and the intermediate confining unit (Pall Aeropower 2009a, 2009b).

Remedial Approach

A two-phase CVOC destruction plan, ISCO followed by augmented reductive dechlorination, was approved by the Florida Department of Environmental Protection and began in 2004. Remediation has focused on in situ destruction of DNAPL and high dissolved concentrations portions of the CVOC plumes. This was the most cost-effective method to destroy contaminant mass and decrease dissolved-phase loading to the plumes, which should then weaken and shorten through natural attenuation.

The low hydraulic conductivity of the site limits the groundwater recovery rate and reagent solution injection rates. As a result, up to 303 permanent treatment wells and 97 direct injection

locations have been used during individual injection events to maximize contact between contaminants and remedial solutions.

- Chemical oxidation using Fenton's reagent was the first step because of its ability to destroy large masses of CVOCs in a short period of time. During three events, approximately 115,000 pounds of 50% hydrogen peroxide (a total of 82,000 gal of hydrogen peroxide and iron solutions) was injected at a rate of 0.75–1.5 gpm. Dissolved TCE destruction typically exceeded 90%.
- Potassium and sodium permanganate are longer-lived chemical oxidants. Twenty-eight thousand pounds of both (98,000 gal of solution) was injected during three events after the majority of the DNAPL and high dissolved concentrations of CVOCs were destroyed and desorption of parent CVOCs from the soil, a relatively slow process, had begun. Residual permanganate ions destroyed CVOCs desorbing from the soil for 6–9 months after injection.
- One hundred fifty-three thousand pounds of emulsified soybean oil (electron donor) and 270 L of proprietary bacteria were injected during four events to enhance and augment reductive dechlorination after chemical oxidation.
- Other solutions were injected to raise the groundwater pH or increase nutrient concentrations to enhance reductive dechlorination.
- Different source areas received different treatments depending on previous contaminant destruction rates and other aquifer parameters. For example, Source Areas 1, 5, and 6 were injected with chemical oxidants once and have received only soybean oil, nutrients, and bacteria since. In contrast, Source Areas 2, 3, and 4 were injected with Fenton's reagent, then soybean oil and bacteria, Fenton's reagent, potassium permanganate, and, finally, soybean oil and bacteria again.

Performance

June 2010 sampling of 92 monitoring wells verified the highest pretreatment TCE concentration (470,000 μ g/L in MW-31D) has been reduced >99.95%. PCE in the same well was reduced 99%. A simultaneous 62% increase in cDCE and a 3770% increase in VC provided evidence that reductive dechlorination is continuing. Overall, though concentrations of daughter compounds, which are more soluble than their parents, have risen in several monitoring wells, total moles of PCE, TCE, cDCE, and VC in the nearly all wells continue to decrease.

Recently, the chlorinated solvent stabilizer 1,4-dioxane was found beneath Source Area 4 at concentrations as high as $63,000 \ \mu g/L$. 1,4-dioxane is also found beneath three of the other five source areas though concentrations do not exceed 320 $\mu g/L$, the natural attenuation default concentration set by Florida Department of Environmental Protection. Pump and ex situ treatment using ultraviolet irradiation and hydrogen peroxide to chemically oxidize the dissolved 1,4-dioxane was chosen as the remedial method because the stabilizer does not adsorb to the soil and recovery and treatment of a pore volume of water should destroy most of the 1,4-dioxane in Source Area 4 in approximately 1 year.

Remedy Evaluation

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. After establishment of suitable conditions, reductive dechlorination, the second remedial method, destroyed contaminants efficiently and for 1–2 years after each Emulsified Oil Substrate[®] injection. Reductive dechlorination is better suited than additional ISCO treatment to reach final cleanup goals for the site. Overall, results to date indicate that the remedial methods and order of application selected in 2004 were appropriate (USEPA 2009).

Outcomes and Challenges

In 2004, the principal responsible party decided to begin remediation immediately rather than await completion of the site assessment. While this decision delayed discovery of the fifth and sixth sources and the fifth plume, it ensured that treatment of the two likely DNAPL source areas began 2–3 years sooner than if a conventional schedule had been followed.

The fifth plume was discovered in 2007. Treatment began in 2008. Prior to that time, only four sources and plumes were treated. Initial treatment of each source and plume with Fenton's reagent greatly reduced the mass in the most contaminated plume and to a lesser degree in three others. Adjustment of groundwater pH and injection of emulsified soybean oil and bacteria in four plumes was within 3 months. Source and Plume 1 has been maintained as enhanced reductive dechlorination since that time with one exception. Sodium permanganate was injected into Plume 1 at a point where PCE and TCE were no longer present and cDCE and VC were the dominant contaminants in October 2009. Sources and Plumes 2–4 and eventually 5 have alternated among Fenton's reagent or potassium permanganate chemical oxidation and augmented reductive dechlorination since. Overall, the treatments appear to have quickly destroyed source mass, converted parent compounds to daughters or ethane/ethene, and greatly reduced plume concentrations.

References and Links

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SITE NAME: PEMACO, MAYWOOD, CALIFORNIA

Contact

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Site Description

Chlorinated and aromatic solvents, oils, flammable liquids, and specialty chemicals were used at the 1.4-acre Pemaco site from the 1940s until June 1991. They were stored in drums and above- and underground storage tanks. USEPA conducted an emergency assessment and stabilization of the area after a 1993 fire.

Both the soil and groundwater at Pemaco are contaminated, and groundwater contamination has migrated off site beneath nearby industrial and residential properties. Plumes in the perched groundwater and the Exposition

Highlight included in Section 4.2.1:

Text Box 4-5. Pemaco, Treatment Transitions

To meet RAOs within 5 years, thermal treatment was used on the highly contaminated soil and groundwater in the source zone. The 2005 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.

Aquifer are discussed below, and the table below shows maximum concentrations of COCs.

Matrix/zone	Compound	Maximum concentration (ppb)	RAO (ppb)
Soil/upper vadose	TCE	3,300	60
	PCE	2,000	-
Soil/lower vadose	TCE	2,100	-
Groundwater/perched	TCE	680	5
	PCE	1,100	5
	1,1-DCE	2,000	6
	VC	240	0.5
Groundwater/Exposition	TCE	22,000	5
	cDCE	14,000	6
	VC	780	0.5

Maximum concentrations and remedial action objectives for COCs at the Pemaco site

Source: USEPA 2005.

- In the surface and near-surface soil, COCs include SVOCs (PAHs) and metals.
- In the perched groundwater, VOC plumes contain primarily TCE, PCE, and VC. The presence of VC is most likely due to TCE/PCE degradation. Multiple "hot spots" exist within

the plumes where VOC concentrations exceed 10,000 μ g/L. Contaminated groundwater extends 250 feet south and 200 feet southwest of the site boundaries. In the perched groundwater, halogenated and nonhalogenated contaminant plumes originating from other former industrial properties adjacent to Pemaco are mixing with the plumes originating at Pemaco (TN&A 2004).

• In the upper zones of the Exposition Aquifer ("A" and "B" zones), a source is creating a contaminant plume of TCE and its degradation products. DNAPL presence is suspected (TCE at greater than 1% of its aqueous solubility); however, the relatively small amount of mass recovered from the source area during ERH treatment indicated that DNAPL was not present at the time of treatment. At its historic maximum, the plume extended laterally over an area measuring 1,300 × 750 feet, and its thickness ranged 1.5–10 feet. TCE was present at a maximum concentration of 22,000 μ g/L (TN&A 2004). Within the >10,000 μ g/L contour of the plume, the average TCE concentration was approximately 16,700 μ g/L (USEPA 2005).

Objectives

The ROD called for groundwater restoration to potential beneficial use as a drinking water source within a remedial action period of 5 years.

Remedial Approach

To meet RAOs within 5 years, thermal treatment was used on the highly contaminated soil and groundwater in the source zone. The 2005 ROD divides the Pemaco site into three subsurface zones. Each zone is described below.

• The "surface and near surface soil remediation zone" extends 0–3 feet bgs, and the selected remedy for this zone is soil cover and revegetation.

Remedial Timeline at Pemaco

- 1991–1999: Emergency removal activities by USEPA, including excavation and removal of drums and above- and underground storage tanks, as well as building demolition.
- 1998–1999: SVE system removed 90,000 pounds of hydrocarbons and solvents from vadose zone soils. The system was shut off due to concerns about dioxin by-product generation.
- 2005: Construction of final remedy begins after ROD is issued in January 2005. City of Maywood begins construction of Maywood Riverfront Park.
- April 2007: Groundwater treatment system begins to operate.
- May 2007: Vapor recovery and treatment system begins to operate. Maywood Riverfront Park completed.
- September 2007–April 2008: ERH applied to source area.
- June 2008: Vapor treatment system permanently switches from flameless thermal oxidation to granular activated carbon due to substantial VOC concentration reductions. *Source*: USEPA 2005, n.d.
- The "upper vadose zone soil and perched groundwater" extends 3–35 feet bgs, and the selected remedy for this zone is high-vacuum dual-phase extraction. This system removes liquid- and gas-phase contamination to address contaminated soil and the perched groundwater plume. Extracted soil vapor was treated with flameless thermal oxidation until VOC concentrations decreased sufficiently to allow vapor treatment via granular activated carbon (GAC). Extracted groundwater is treated on site using a GAC/ultraviolet oxidation unit.

• The "lower vadose zone soil and Exposition zone groundwater" extends 35–100 feet bgs. This is considered the source area of the site; the most highly contaminated soil is found here, as well as the dissolved phase Exposition zone groundwater plume. The selected remedy for this zone is ERH with vapor extraction, vacuum-enhanced groundwater extraction, and groundwater P&T, followed by MNA. The ROD stated that ERH would be applied within the 10,000 μ g/L TCE groundwater contour, with electrodes installed as deep as 100 feet bgs. The design report amended the contour, expanding the heating area to include a 4,000 μ g/L contour. The ERH treatment area was approximately 14,000 square feet. Thirty thousand cubic yards of material was treated in the Exposition A and B zones, 30–95 feet bgs. A flameless thermal oxidation unit was used to treat vapor, while groundwater was treated with GAC/ultraviolet oxidation (USEPA n.d.).

Construction was completed in September 2007. The ERH system was applied to the source area for approximately 6 months in conjunction with the vapor and groundwater extraction and treatment system.

Performance

The initial TCE mass estimate in the ERH target zone ranged 96–106 pounds. Pre-ERH groundwater pumping removed 70% of the dissolved TCE mass in this area. The remaining 30% was extracted during ERH, amounting to approximately 31.5 pounds of TCE in the vapor phase and 9 pounds of TCE in groundwater (TN&A 2009).

The small amount of mass removal indicates that no DNAPL was present in the source area at the time of treatment. Despite a relatively small amount of recovered contaminant mass, groundwater and soil TCE concentrations in the ERH area decreased by over 99% (TN&A 2009).

Since USEPA turned off the ERH system in April 2008, contaminant concentrations in the source area, dissolved-phase plumes, and vapor have declined steadily (USEPA n.d.). COC concentrations are now below remedial goals in several monitoring locations. The ERH treatment is considered to be a success. For example, in Exposition Zone B and the area immediately surrounding the treatment zone, July 2010 monitoring data shows TCE groundwater concentrations are below MCLs in 11 out of 18 monitoring wells (USEPA 2010).

- Of the 11 wells that meet MCLs, the range of current TCE concentrations is $0.5-5 \mu g/L$. Pre-ERH concentrations in these wells ranged $100-4600 \mu g/L$.
- Of the seven wells that do not meet MCLs, the range of current TCE concentrations is $5.2-190 \mu g/L$. Only three wells are above $25 \mu g/L$. Pre-ERH concentrations in these wells ranged $170-2900 \mu g/L$.

Almost all post-ERH soil samples taken from the treatment area in November 2008 exhibited TCE concentrations significantly below 60 μ g/kg (TN&A 2008). Almost all concentrations are below 10 μ g/kg. Pre-ERH concentrations in these wells were typically on the scale of hundreds or thousands of μ g/kg.

Remedy Evaluation

Significant reductions in VOC levels have been achieved in other contaminated areas of the site due to groundwater pumping and dual-phase extraction. A total of 14,584 pounds of VOCs has been removed site-wide, including a substantial amount of hexane and other light-end hydrocarbons. Groundwater pumping and monitoring are ongoing at Pemaco.

At the Pemaco Superfund site, ERH technology was used to address a CVOC source zone. Initial concentrations of TCE in the source zone were as high as 22,000 μ g/L. After 6 months of thermal treatment, TCE concentrations fell below MCLs in several monitoring wells, and other wells exhibit significant concentration reductions.

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SITE NAME: WESTERN PROCESSING, KING COUNTY, WASHINGTON

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Site Description

Due to improper waste storage/disposal and spills at the Western Processing Site, site soils, shallow groundwater, and Mill Creek became contaminated with more than 90 of USEPA's

Highlight included in Section 6.3.3.1:

Text Box 6-4. Western Processing, Changing Direction after No Recognizable Benefit

After 8 years of aggressive efforts to restore the groundwater to acceptable levels via P&T and surface water infiltration, USEPA changed the remedy to containment in December 1995 for the following reasons:

- The chlorinated-solvent plume had a continual DNAPL source.
- O&M costs for the P&T system were prohibitively high.
- Monitoring showed that the plume was naturally attenuating outside the slurry wall.

priority pollutants. The primary categories of contaminants at this site are VOCs, SVOCs, and heavy metals. Organic COCs at this site include TCE, cDCE, *trans*-DCE, dichloromethane, toluene, and chloroethene. DCE concentrations detected in groundwater are greater than 6% of the compound's aqueous solubility, indicating that DNAPL is likely present in the subsurface (USEPA 1998). The water table begins 5–20 feet bgs, and over 95% of all contamination at the site is located in the uppermost 15 feet of soil. The table below shows historical VOC concentrations.

	1988	1995	1992	2002	2003	2005	2006	2007	2008	MCL
TCE			ND^b	ND	ND	ND	ND	ND	ND	5
cDCE	>2000	<100			ND	ND	ND	ND	ND	70
Chloroethene				150 ^c		<16 ^d	<16 ^d	ND	ND	2

"Trans" plume concentration reductions at the Western Processing Site $(\mu g/L)^a$

^{*a*} A blank cell indicates that information was not readily available. The plume primarily contained cDCE when it was initially discovered in 1988.

^{*b*} ND = nondetect.

^c Detected in six wells.

^d Detected in one well.

Sources: USEPA 1998, 2008.

Groundwater contamination on site primarily affected the shallow groundwater (top of water table to 30–40 feet bgs) in the uppermost hydrogeologic zone (Zone A). The volume of the shallow, on-site plume, consisting of a wide variety of contaminants, was estimated at 500 million gallons in 1987 (USEPA 1998). However, contamination also reached the second hydrogeologic zone (Zone B), which extends to 80 feet bgs. In 1986 an off-site plume, consisting of what was thought to be *trans*-1,2-DCE, was discovered. This plume, referred to as the "trans" plume, had migrated underneath Mill Creek and extended just west of it. The primary compound in the plume was later determined to be cDCE; however, it is still referred to in site documents as the "trans" plume. No drinking water sources have been affected by this site.

Objectives

See table above.

Remedial Approach

The site has been divided into four sectors (see figure). Sector 3 refers to the "trans" plume. Surface cleanup was completed in 1984 as part of the Phase I removal action. In 1988, two P&T systems began to operate, and a 40-foot-deep slurry wall was constructed around the site. On- and off-site P&T systems were installed to contain groundwater contamination within site boundaries and produce an within the slurry upward flow wall/source area. shallow А groundwater extraction/infiltration system and a "trans" plume extraction system were also constructed in 1988.

After 8 years of aggressive efforts to restore the groundwater to acceptable levels via P&T and surface water infiltration, USEPA changed the remedy to containment in December 1995 for the following reasons:



Western Processing Site map. Source: EPA 2008.

- The chlorinated-solvent plume had a continual DNAPL source.
- Prohibitively high operations and maintenance costs for the P&T system.
- Monitoring showed that the plume was naturally attenuating outside the slurry wall.

Since then, the following remedial activities have occurred:

- 1996: New, more automated extraction system was installed to contain on-site and off-site plumes.
- 1997: Hot spots were excavated, treated, and backfilled.
- 1997: An isolation wall was constructed around Sector 4 because it has relatively low contamination; this reduced the amount of groundwater pumping.
- 1999: A RCRA cap was placed over the containment area (Sector 1) to reduce infiltration to subsequently the amount of pumping.
- 1999: Evaluation of geochemical indicators shows that proper conditions for natural degradation of "trans" plume exist.
- 2000: Extraction wells in Sector 3 were turned off and MNA was used for the "trans" plume.

Performance

Since 1990 the surface water in Mill Creek has met Federal Ambient Water Quality Criteria, indicating that the shallow groundwater is sufficiently clean. Maintaining an inward groundwater flow from Zone B to Zone A within the slurry wall has also been met.

Indications of "Trans" Plume Breakdown

- TCE has not been detected since 1992.
- 1,2-DCE has not been detected since 2002.
- Chloroethene (VC) has not been detected since 2006.

Source: EPA 2008.

Significant improvements have been made in the "trans" plume area since the MNA program began in 2000. The off-site VOC plume currently extends in a northwest direction from the southwest portion of the site. Both the size of this plume and its VOC concentrations continue to steadily decrease. The plume is biodegrading to well below MCLs (USEPA 2008).

Geochemical indicators such as redox potential, dissolved iron, VOCs, methane, ethane, and ethene continue to be monitored to ensure that proper geochemical reducing conditions exist in Sector 3. USEPA (2008) stated, "Geochemical sampling continues to support that conditions in the trans plume area are conducive to the natural breakdown of vinyl chloride (chloroethene); sampling results appear to verify that this breakdown is occurring as expected."

The Western Processing Site is currently in the long-term O&M phase. The slurry wall has cut off the chlorinated-solvent plumes and has isolated the contaminant mass. The P&T and MNA program has reduced the groundwater concentration outside the slurry wall to nondetectable levels. The new containment strategy has made it possible for the P&T system to operate at a much lower rate while still containing onsite contamination. As a result, annual operating costs have fallen from \$5 million to approximately \$600,000. USEPA has determined that current human exposure pathways and groundwater migration for the site are under control (USEPA 2008).

Remedy Evaluation

A cDCE plume is currently biodegrading to well below MCLs at the Western Processing Site under an MNA program coupled with a slurry wall that cut off the source of the plume. As cDCE (a daughter product of TCE) degrades to ethene, it produces an intermediate, carcinogenic compound—VC. For this reason MNA remedies backfire if the natural groundwater conditions are unable to completely dechlorinate intermediate compounds to the end compound, ethene. Now that the contaminant source has been isolated at the Western Processing Site, MNA appears to be completely degrading contaminants in the groundwater plume with no detections of intermediate compounds in the plume area since 2006.

References and Links

USEPA (U.S. Environmental Protection Agency). 1998. Pump and Treat of Contaminated Groundwater at the Western Processing Superfund Site, Kent, Washington. http://costperformance.org/pdf/Western_Processing.pdf. USEPA. 2008. Fourth Five-Year Review Report for Western Processing Superfund Site. www.epa.gov/superfund/sites/fiveyear/f2008100002609.pdf.

Appendix B

Developing an IDSS

DEVELOPING AN IDSS

As described in Chapters 2–5 of this guidance, the four elements of developing an IDSS for chlorinated solvent sources and plumes include the following:

- conceptual site model based on reliable characterization methods and an understanding of the subsurface conditions that control contaminant movement and distribution
- remedial objectives and performance metrics, based on realistic assumptions and expectations
- treatment technologies applied in sequence or in parallel, based on each one's optimal niche and potential synergistic effects
- monitoring strategies based on interim and final cleanup objectives, the selected treatment technology and approach, and the remedial performance goals

This appendix applies each of these four elements to a more complex example site (modified from an example in Sale and Newell 2011) to illustrate how each contributes information to the development of an IDSS. At the end of the example, alternative outcomes are presented to illustrate how changes to a limited number of parameters may change the outcome, illustrating the flexibility of the IDSS process in developing alternative solutions.

B.1 Site Description

The site in this example is a large industrial facility where piping on a storage tank failed, allowing the rapid release of approximately 10,000 gal PCE into a thick, highly heterogeneous alluvial fan deposit containing interbeds of moderately to poorly sorted silt, fine sand, and coarse sand. Residual DNAPL, representing nearly 60% of the original release, still resides in the vadose zone and groundwater beneath and near the source area. Over a period of 20 years, a groundwater contamination plume developed and extended from the release area downgradient across the industrial property and into an adjacent residential neighborhood. The release has caused or may cause a number of adverse or potentially adverse exposures that must be addressed, including the following:

- The concentrations of PCE in the groundwater and vadose zone at the industrial site, when modeled, indicate a potential adverse vapor intrusion exposure to workers in buildings overlying and near the source area and above the groundwater contamination.
- The industrial facility receives its water supply from a well on the property in which PCE concentrations exceed drinking water standards.
- The area of the spill is currently not occupied, and therefore direct exposure to the contamination in that area does not occur.
- Modeling of the potential for vapor intrusion of VOCs from groundwater in the residential area off site has shown that there is a potential for indoor air to contain concentrations of VOCs above a de minimus level $(1 \times 10^{-6}$ incremental cancer risk and hazard index of 1).
- PCE concentrations exceed the drinking water standard (5 μ g/l) in groundwater contamination plume. In addition, VOCs exceed drinking water standards in a water supply
well within the downgradient plume. There are no other water supply wells within the plume area or within 2 miles of the leading edge of the plume.

These real and potential exposures are incorporated into the CSM and used to establish functional objectives as presented below.

B.2 Site Conceptual Model

Figure B-1 provides plan view and cross-sectional representations of the site. The source area and plume are approximately 4400 feet long. The top of the water table is 20 feet bgs. The depth to the base of PCE contamination varies 40–60 feet bgs. The plume is aerobic, and the absence of PCE degradation products suggests that there is little, if any, natural degradation of PCE occurring. The apparent transport velocity of the plume is 1 mile in 20 years, or approximately 260 feet/year. The attenuation of aqueous-phase PCE concentrations with distance is attributed to the combined effects of sorption in transmissive zones and storage of dissolved- and sorbed-phase contaminant in low-permeability zones. Contaminant storage in low-permeability zones is shown graphically by low-permeability interbeds (lenses with dashes) that have higher concentrations at their margins than in their interiors. The figure legend defines the aqueous-phase equivalent concentrations represented in figure. See Section 2.5.2 for a description of the use of aqueous-phase equivalents to represent conceptualized distribution of contaminants using the 14-Compartment Model.





Figure B-1. Plan view and cross-sectional representation of example site.

Figure B-1 splits the release into a source zone, an on-site plume, and an off-site plume. The subdivision of the plume is necessitated because of different on- and off-site exposure scenarios, accessibility, plume concentrations, absolute and functional objectives.

B.3 Mapping Contaminant Distribution and Fluxes

Figure B-2 uses the 14-Compartment Model to depict aqueous-phase contaminant distribution and contaminant concentration in orders of magnitude as defined in the Figure B-1 legend (aqueous-phase equivalent as described in Chapter 2). According to Section 2.4.1, this site is a middle-stage site. Note that the 14-Compartment representation in Figure B-2 has been modified to include separate sets of transmissive and low-permeability compartments for the on- and offsite plumes. The aqueous- and vapor-phase concentrations in transmissive zones in Figure B-2 were developed from available water quality and soil gas data. The concentrations in the remaining compartments were based on anticipated partitioning among the four phases (arrows) and between the transmissive and low-permeability zones per the processes described in Chapter 2. Unfortunately, as is typical of many sites, no data were available from low-permeability zones. Thus, development of a 14-Compartment Model can help identify critical data gaps (e.g., improved mass distribution) and decisions regarding collection of additional data. Figure B-2 also shows the critical points where human exposure most likely will occur (off-site indoor air depicted by the house icon and on- and off-site drinking water well depicted by the well icon).



Figure B-2. Plan view and cross-sectional representation with 14-Compartment mapping of the example site. *Source*: Modified from Sale and Newell 2011.

B.4 Site Remedial Objectives

The next step in IDSS development is to create a set of absolute and functional objectives for the site (see Chapter 3). For this example the key drivers for all parties are as follows:

- Locally, home owners in the residential area are concerned about potential health effects, potential impacts to property values, and disruptions in the neighborhood.
- Regionally, the community is committed to a clean environment while wanting to preserve jobs.
- The facility owners are committed to immediate disruption of any completed exposure pathways and meeting all other obligations through actions that have consequential benefits, are economically feasible, and have low O&M costs.
- Regulators wish to support the interests of the community, provide technical support to all parties, and achieve compliance with applicable rules and regulations.

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

- Protect human health and the environment.
- Address adverse community impacts.
- Minimize the burden of past practices on future generations.
- Conserve natural resources.
- Apply resources effectively and efficiently.

Table B-1 lists site-wide <u>hypothetical</u> functional objectives supporting these five absolute objectives. Columns to the right of the functional objectives provide a basis for a qualitative

ranking, based on Qualitative Performance Estimates (QPEs), defined Text Box B-1, of how well an action or set of actions meets the functional objective in the "short" term (a few years) or "long" term (a decade or more). Included as an option is "no clear benefit." For this example, the status quo (no clear benefit) includes no active groundwater use and vapor mitigation beneath homes which exceed indoor air standards. Pragmatically, any new set of actions should result in a consequential improvement over the status quo.



At this point, the functional objectives have not yet been assigned SMART attributes. Applying the SMART criteria to the functional objectives requires that we limit the SMART application to those functional objectives that require action to drive the remediation toward protection of human health and environment (see real or potential exposure in Section B.1). Those functional objectives are highlighted in light blue in Table B-1. As discussed in Chapter 3, the remaining functional objectives in Table B-1 are not discarded but are considered in the development of SMART Functional Objectives 1, 2, 3, and 6. Section B.5 describes the process followed to ensure that Functional Objective 1, 2, 3, and 6 are modified to accommodate the SMART attributes.

Functional			is quo				
objectives	Term in which the result is anticipated	Short	Long				
	Absolute objective: Protect human health and the environment—Risk						
1	Prevent adverse human exposure via groundwater given current and reasonable future use (off site).	С	C				
2	Prevent adverse human exposure via soil gas given current and reasonable future use (off site).	С	В				
3	Prevent adverse worker-related exposures via soil, groundwater, and/or soil vapor (on site).	С	В				
4	Avoid actions that have the potential to increase risk.	С	В				
	Absolute objective: Protect human health and the environment—Extent						
5	Prevent expansion of plumes.	С	C				
6	Reduce the extent of plumes.	С	С				
	Absolute objective: Protect human health and the environment—Longevity						
7	Reduce the period in which persistent releases to groundwater occur.	С	С				
8	Reduce the period in which releases to soil gas occur.	С	С				
	Absolute objective: Protect human health and the environment—Regulatory						
9	Comply with local, state, and federal regulations.	С	C				
	Absolute objective: Address adverse community impacts—Community						
10	Avoid undue interruptions to community.	A	A				
	Absolute objective: Minimize the burden of past practices on future generations—Land use						
11	Restore beneficial use of impacted lands.	С	C				
	Absolute objective: Apply resources effectively and efficiently—Economic						
12	Select actions that have a practical near-term capital cost and minimal life-cycle cost.	В	В				
	Absolute objective: Apply resources effectively and efficiently—Sustainability						
13	Select measures that have a net positive environmental benefit.	С	С				
14	Avoid undue remedy-related interruptions to communities, government, and industry activities.	Α	Α				
	Absolute objective: Minimize the burden of past practices on future generations—Resource conserv	vation					
15	Limit future degradation of natural resources.	С	С				
16	Restore impacted groundwater to standards needed for beneficial use.	С	С				
	Absolute objective: Apply resources effectively and efficiently—Implementations						
17	Select remedies that are practical to install.	A	Α				

 Table B-1. Comprehensive functional objectives and qualitative performance estimates (see Text Box B-1)

SMART Objectives

The functional objectives described in Table B-1 are still general. As described in Chapter 3, functional objectives should meet the SMART attributes. Development of SMART attributes for each functional objective more accurately describe the potential for successful remediation of part or all of the contaminated site. Development of SMART functional objectives is difficult and dependent on the reliability of the CSM. Attempting to make all functional objectives in Table B-1 "SMART" is probably impractical in this example. This exercise is limited to those objectives that directly contribute to site remediation. Accordingly, Functional Objectives 1, 2, 3, and 6 are selected as to illustrate the process for applying the SMART attributes.

Making functional objectives SMART often requires that the objective be revised and/or divided into interim functional objectives and final functional objectives. For example, the team of stakeholders originally defined four functional objectives in support of Absolute Objective #1 (i.e., To protect human health and environment) as follows:

- 1. Prevent adverse human health exposure off site via groundwater given current and reasonable future use.
- 2. Prevent adverse exposure off site via soil gas given current and probable future use.
- 3. Prevent adverse on-site worker-related exposure via soil, groundwater, and/or soil gas.
- 4. Reduce the extent of the plume.

As SMART attributes are developed for each functional objective, the objectives are further refined into interim functional objectives (see Table B-2). The SMART interim functional objectives clearly define specific, measureable, attainable, relevant, and time-bound objectives from the immediate time frame through the 20-year remediation schedule. This procedure allows interim reviews of performance to evaluate trends early in the remediation process (2 years) rather than waiting 20 years to determine success or under performance.

Table B-2 illustrates that the four functional objectives each require three to four interim objectives to address separate time-bound elements or allow shorter-term measurement of success. Each interim functional objective contributes to the completion of the final functional objective, and each final functional objective contributes to the completion of the absolute objective, which is to protect human health and the environment.

Table B-2 provides a checklist of positive answers to the consideration of SMART attributes for Functional Objectives 1, 2, 3, and 6. The determination that they do or do not adhere to SMART attributes requires a short description of the basis for that determination. Text Box B-3 documents this basis for claiming SMART attributes apply to each final functional objective.

Absolute objective—Protect human health and the environmer	nt						
			SMART attri	butes			
Functional objectives	(Yes/No)						
	Specific	Measureable	Attainable	Relevant	Time-bound		
	Risk						
 Prevent adverse human exposure via off-site groundwater given current and future reasonable use. Interim functional objective—Immediately provide alternative water supply and/or provide treatment on existing water supply well until concentrations are reduced to below the drinking water standard. Interim functional objective—Show a positive trend towards achieving the final functional objective within 2 years. Interim functional objective—Provide groundwater monitoring program to allow periodic assessment of groundwater plume within 6 months. Final functional objective—Reduce PCE mass flux at the property boundary to allow the concentrations in off-site groundwater to be reduced to below the drinking water standard within 20 years (3.0 OoM reduction in flux). 	Yes	Yes	Yes	Yes	2/20 years		
 Prevent adverse exposure off site via soil gas given current and future reuse. Interim functional objective—Within 6 months measure soil vapor, and potentially indoor air, off site to determine whether an adverse exposure potentially exists. Interim functional objective—Within 6 months develop a contingency plan that will mitigate any adverse exposures due to soil vapor determined by results of sampling. Implement the plan as needed. Interim functional objective—Within 6 months develop a monitoring program to assess soil vapor concentrations over time and allow periodic assessment of soil vapor risk. Implement the plan. 	Yes	Yes	Yes	Yes	6 months		

Table B-2. Functional objectives for complex example site

Absolute objective—Protect human health and the environment	nt						
			SMART attri	butes			
Functional objectives	(Yes/No)						
	Specific	Measureable	Attainable	Relevant	Time-bound		
 3. Prevent adverse on-site worker-related exposure via soil, groundwater, and/or soil gas. Interim functional objective—Immediately provide interim alternative source of drinking water for workers until a permanent replacement is made or treatment provided on existing well. Interim functional objective—Provide permanent replacement or wellhead treatment on existing well within 1 year. Interim functional objective—Immediately provide training to workers to inform them of the potential risks from soil and soil vapor contamination. Interim functional objective—Immediately provide mitigation to prevent the adverse exposures to workers. 	Yes	Yes	Yes	Yes	Immediately		
 4. Reduce the extent of the plume. Interim functional objective—Provide containment of the source area in the vadose within 1 year. Interim functional objective—Provide mitigation to reduce the flux of contamination at the property boundary by 3 OoMs within 2 years. Final functional objective—Deplete the mass in the contained source area. 	Yes	Yes	Yes	Yes	Containment within 1 year. Reduce mass flux in 2 years. Deplete mass using addition of electron acceptor, 5-year reviews, 20-year completion.		

Table B-2. Functional objectives for complex example site

Text Box B-3. SMART Attributes for Functional Objectives

ABSOLUTE OBJECTIVE—PROTECT HUMAN HEALTH AND THE ENVIRONMENT

- **Functional Objective #1**—Prevent adverse human exposure off site via groundwater given current and reasonable future use [Prevent adverse human exposure via groundwater].
 - Specific—The property boundary is defined, alternative source of water supply provided, reduce concentration to below drinking water standard in 20 years, and the level of reduction (mass discharge) is defined as 3 OoMs.
 - Measurable—Mass discharge (M_d) can be measured before treatment begins and periodically thereafter to establish a trend in 2 years (see Chapter 5). Groundwater monitoring required to provide periodic measurements.
 - Attainable—Given subsurface characteristics, contaminant concentrations, and plume dimensions, the objective appears achievable.
 - Relevant—The objective is relevant to the current and desired use of the resource, e.g., industrial and residential land use.
 - Time-bound—Two years is an interim time constraint to assess the trend of mass reduction using M_d measurements; 20 years is the final time constraint where the compliance point at the boundary between industrial use and residential use must meet drinking waster criteria.
- **Functional Objective #2**—Prevent adverse human exposure off site via soil gas given current and reasonable future use.
 - Specific—Design, install, and operate a soil gas monitoring system to evaluate potential for exposure; provide mitigation measures if there is an unwanted exposure.
 - Measureable—Indoor air testing would be based upon soil gas results.
 - Attainable—A well-designed and operated monitoring system should identify gas migration and potential exposure.
 - Relevant—Protection of human health is relevant.
 - Time-bound—System design and implementation and any necessary mitigation are time-bound.
- Functional Objective # 3—Prevent adverse on-site worker-related exposures via soil, groundwater, and/or soil vapor.
 - Specific—Provide alternative source of water; provide training on potential adverse exposures; provide mitigation for those exposures that cannot be avoided.
 - Measureable—Property is owned by the company so it can self-regulate/measure compliance with administrative controls–Occupational Safety and Health Administration requirements.
 - Attainable—Company owns and controls the property.
 - Relevant—Worker health and safety are protected and relevant.
 - Time-bound—Immediate.
- Functional Objective #6—Reduce the extent of plumes.
 - Specific—3 OoMs decrease in aqueous concentration needed for no impact, from 1000s of μg/L down to <10 μg/L.
 - Measureable—M_d at the downgradient edge of the source zone over time; groundwater monitoring to assess extent of plume.
 - Attainable—Yes, but system operation will be very dependent on the sorbed contaminant in the transmissive zones and the stored contaminant in the low-K zones.
 - Relevant—Long-term project to protect the drinking water system without wellhead maintenance and to protect the resource as a whole.
 - o Time-bound—5-year reviews will be used to measure rate of change and evaluate progress

During implementation, failing to achieve any of the interim functional objectives (e.g., show a positive trend toward achieving the final functional objectives within 2 years) or final Functional Objective #1 (e.g., reduce PCE mass flux at the property boundary to allow the concentrations in off-site groundwater to be reduced to below the drinking water standard within 20 years

(3.0 OoMs reduction in flux) provides data by which the original decision is reevaluated or, more importantly, the functional objective is refined. Failing to achieve an interim or final functional objective triggers an evaluation of the information known before remediation began, the assumptions regarding the site or the remedial design, and the performance predictions for the original remedial approach. It may become clear that the CSM needs additional detail (Chapter 2) or the technology(ies) may need to transition to another technology or technology combination (Chapter 4) to improve treatment performance before modification of the functional objective is considered. Regardless, it is likely that the additional information gathered since the original functional objectives were established and the original remedial actions or treatments were developed will change the original CSM, which in turn will identify remedial design or operational inadequacies.

B.5 Development of Remedial Measures

Selection of remedial measures is an iterative process where options are proposed, performance is predicted, and complementary measures are added to address limitations of the basic method. The first step in this process is development of a "first cut" set of actions (remedies) that will likely be employed and, conversely, other actions that are unlikely. For this example, elements that are likely and unlikely include the following:

Likely:

- land use restrictions that preclude future use of groundwater in the impacted area for the foreseeable future (Functional Objectives 1 and 3)
- maintenance of vapor mitigation at all homes where a potential for adverse impacts related to the site exists (Functional Objective 2)
- long-term monitoring to verify the continued protectiveness of the site remedy
- continuing supply of an alternative source of water or treatment of existing contaminated supplies, both on and off site, until contaminant concentrations allow use of the water once again (Functional Objective 1)
- maintaining mitigation measures designed to protect on-site workers from adverse exposure to contaminants in soil and soil vapor (Functional Objective 3)

Unlikely:

- measures that would preclude continuing habitation of impacted homes
- measures that would cause the industrial facility to close

For this example, we assume that the interested parties propose two divergent options for dealing with the source area:

- source depletion via in situ thermal treatment
- source containment via a bentonite slurry wall and low-flow hydraulic containment

Figure B-3 predicts the outcome of source depletion. The anticipated performance is based on the conditions identified in Figure B-2 and a map of technology performance for in situ conductive heating in Figure B-3. One variation is the predicted result that an order-of-

magnitude reduction in aqueous concentrations in transmissive zones in the plume will yield 1 OoM reduction in vapor concentrations in transmissive zones of the on-site plume, reinforcing the fact that anticipated performances for technologies are guides (see Section 4.1.1), not fixed results.



Figure B-3. Near-term (~5 years) effect of source depletion via in situ conductive heating. Source: Modified from Sale and Newell (2011), Figure 46.

Figure B-4 predicts the outcome for source containment. Anticipated performance is based on the conditions identified in Figure B-2 and application of bentonite slurry walls and low-flow pumping. From a performance perspective, the primary difference between the two options is that thermal treatment depletes the source, while containment and pumping has little effect on contaminants in the source zone. From an order-of-magnitude perspective, both options have similar results in on- and off-site plumes. Table B-3 provides further insights regarding the merits of the options.

Other differences between the options are that thermal treatment may have a higher initial capital investment yet shorter treatment period, resulting in a lower life-cycle cost, and may disrupt site activities during the first year (see Chapter 4). Conversely, containment and hydraulic control may have a higher life-cycle cost and extended liability due to long-term O&M. Containment will also cause site disruption during barrier installation (first year) and maintenance (out years). Containment will also be an obstacle to construction of site infrastructure that would cross the barrier itself. A limitation of both source depletion and source containment is that any downgradient effect is slow and difficult to predict, and only gradual improvement in aqueous and vapor concentrations in the off-site plume will be achieved.



Figure B-4. Near-term (~5 years) effect of source containment via a bentonite slurry wall and low-flow hydraulic containment. *Source*: Modified from Sale and Newell (2011), Figure 47.

Considering the analysis in Table B-3, modifications to the thermal source treatment and containment include the following:

- An iron PRB (Section 4.1.4.3) can be added at the downgradient edge of the on-site plume. This can be expected to reduce the time required to realize improvements in aqueous- and vapor-phase concentrations in the off-site (residential) plume. The iron PRB can complement either the thermal or containment options.
- An electron donor (e.g., emulsified vegetable oil ISB, Section 4.1.3.3) can be injected upgradient of the bentonite slurry wall. Biological treatment can be expected to reduce or even eliminate ongoing hydraulic controls inside the containment zone and, in the long term, reduce contaminant concentrations in the source zone.

Table B-3. Example 1—Analysis of the status quo, thermal treatment of the source, and
containment of the source

	State que					l Containment	
Functional objectives	Term in which the result is anticipated	Long	Short	Long	Short	Long	
	Risk						
1	Prevent adverse human exposure via groundwater given current and reasonable future use.	С	С	В	В	В	В
2	Prevent adverse human exposure via soil gas given current and reasonable future use.	С	В	В	А	В	А
3	Prevent adverse worker-related exposures via soil, groundwater, and/or soil vapor.	С	В	В	A	В	А
4	Avoid actions that have the potential to increase risk.	С	В	В	Α	В	Α
	Extent					-	_
5	Prevent expansion of plumes.	С	С	С	В	С	В
6	Reduce the extent of plumes.	С	C	С	В	С	В
	Longevity					-	
7	Reduce the period in which persistent releases to groundwater occur.	С	C	С	В	C	В
8	Reduce the period in which releases to soils gas occur.	С	C	С	В	С	В
	Regulatory						
9	Comply with local, state, and federal regulations.	С	C	C	C	С	С
	Community					•	
10	Avoid undue interruptions to community.	Α	A	A	A	Α	Α
	Land use						
11	Restore beneficial use of impacted lands.	С	C	C	В	С	В
	Economic						
12	Select actions that have a practical near-term capital cost and minimal life-cycle cost.	В	В	D	А	А	D
	Sustainability						
13	Select measures that have a net positive environmental benefit.	C	C	C	В	В	В
14	Avoid undue remedy-related interruptions to communities, government, and industry activities.	A	A	В	В	А	А
	Resource Conservation						
15	Limit future degradation of natural resources.	С	C	В	В	В	В
16	Restore impacted groundwater to standards needed for beneficial use.	С	С	C	C	C	C
	Implementations						
17	Select remedies that are practical to install.	A	A	В	В	Α	Α

With these modifications to the IDSS system, the performance of both options remains similar within an order of magnitude. Figure B-5 predicts the outcome of enhanced options, referred to as Containment Plus (electron donor and PRB) and Thermal Plus (PRB). This estimates a 1 OoM improvement in the transmissive zone of the off-site plume. It does not address the potential exposure to on-site workers; therefore, land reuse and the on-site drinking water well remain a long-term issue to be resolved and can affect the value of the industrial complex. Lastly, Table B-4 compares the expected performance for the status quo, Thermal Plus, and

Containment Plus. Similar outcomes are expected for both options; however, Containment Plus should have a lower initial capital cost and better accommodate the ongoing industrial land use.



Figure B-5. Near-term (~5 year) effect of source containment via a bentonite slurry wall, PRB, and addition of an electron acceptor inside the slurry wall. Source: Modified from Sale and Newell (2010).

More active treatment of the off-site plume is possible; however, higher off-site activity levels may disrupt or even alarm off-site residents. Conversely, less-active treatment may require an extension of the 20-year projected completion date for protection of the off-site drinking water well. However, it must be acknowledged that predications beyond 20 years can be unreliable, and our knowledge base is constantly changing (see Chapter 3).

		Sta	tus	Thermal		Containment	
Functional objectives	Term in which the result is anticipated	Short	Long	Short	Long	Short	Long
	Risk						
1	Prevent adverse human exposure via groundwater given current and reasonable future use.	С	C	В	А	В	А
2	Prevent adverse human exposure via soil gas given current and reasonable future use.	С	В	В	А	В	А
3	Prevent adverse worker-related exposures via soil, groundwater, and/or soil vapor.	С	В	В	A	В	А
4	Avoid actions that have the potential to increase risk.	С	В	В	Α	В	Α
	Extent						
5	Prevent expansion of plumes.	С	C	В	Α	В	Α
6	Reduce the extent of plumes.	С	С	В	Α	В	Α
	Longevity					-	
7	Reduce the period in which persistent releases to groundwater occur.	С	С	В	А	В	А
8	Reduce the period in which releases to soils gas occur.	С	С	В	Α	В	А
	Regulatory						
9	Comply with local, state, and federal regulations.	С	C	C	В	С	В
	Community						
10	Avoid undue interruptions to community.	Α	Α	Α	Α	А	А
	Land use						
11	Restore beneficial use of impacted lands.	С	C	В	Α	В	А
	Economic		-				
12	Select actions that have a practical near-term capital cost and minimal life-cycle cost.	В	В	D	А	А	А
	Sustainability						
13	Select measures that have a net positive environmental benefit.	C	C	C	В	В	В
14	Avoid undue remedy-related interruptions to communities, government, and industry activities.	A	A	В	В	А	А
	Resource Conservation						
15	Limit future degradation of natural resources.	C	C	В	Α	В	А
16	Restore impacted groundwater to standards needed for beneficial use.	С	С	С	В	C	В
	Implementations						
17	Select remedies that are practical to install.	Α	A	В	В	Α	Α

Table B-4. Example 1—Analysis of the status quo, thermal plus, and containment plus

Initial Mapping Summary

Remedial measures were developed through an iterative process. Outcomes of the proposed actions were predicted for all approaches using the 14-Compartment Model. Both approaches provide substantial improvements over the status quo with respect to imminent or already completed exposure pathways. At the same time, the slurry wall containment and treatment option leaves contaminants in places that will be addressed only by historically slow natural

attenuation processes. In the end, this solution can be implemented only if all stakeholders agree on the value of what will be achieved versus the cost to manage the risks that remain.

B.6 Reevaluating an Underperforming Site Strategy

The example explored in Chapter 6 is used below to illustrate how an underperforming remedy is reevaluated using the process described earlier in this chapter. From Chapter 6, after semiannual monitoring of the "containment plus" remedial option (see Text Box B-4), results from the source are as follows:

• TCE (the primary source contaminant) is still present at 1%–5% of solubility a concentration indicative of the presence of DNAPL (Figure B-6 shows both lowpermeability and transmissive zones are still above

Text Box B-4. Containment Plus Remedial Option (see Figure B-5)

A bentonite slurry wall was emplaced and has been operational for 4 years in addition to the low-flow hydraulic containment system. Emulsified vegetable oil was injected into the subsurface within the containment wall to accelerate treatment. A downgradient ZVI PRB was put in place ~3.5 years ago.

100s of μ g/L TCE), though DNAPL, once frequently observed, has not been detected for more than 2 years.

• Concentrations of TCE have been monitored quarterly in groundwater from the low-flow hydrodynamic control that backs up the slurry wall. However, monitoring events coinciding with two periods of excessive precipitation, there has been no observable TCE detected.



Figure B-6. Modified from Figure B-5 to illustrate the potential existence of DNAPL.

Results within the downgradient dissolved plume indicate the following:

- COC trends upgradient of the PRB initially showed a substantial decline but have been at persistent, relatively low concentrations (<0.5 ppb) over the last 2 years.
- COC trends in groundwater immediately downgradient of the PRB have been substantially reduced and are currently not detected.
- However, COC concentrations at the distal portion of the plume downgradient of the PRB have largely remained unchanged, likely due to back diffusion (see Figure B-6). Aqueous concentrations in this area remain at 10s of μ g/L TCE.

B.7 Response to an Underperforming Remedy

The functional objective for human exposure to off-site groundwater contaminated with TCE (Functional Objective #1, Table 3-1) is predicated on a 20-year treatment time frame for full compliance, with an interim time frame of 2 years to demonstrate a positive trend toward drinking water criteria. Given that the groundwater velocity has been estimated at approximately 260 feet/year and the distance from the PRB to the compliance monitoring point is approximately 3000 feet, the impact of the PRB would not be seen downgradient in less than 11–12 years without the exacerbating effects of back-diffusion and desorption.

Four years is not sufficient for any changes due to treatment to be seen at the compliance well. However, given the long period of time between treatment and observations at the compliance well, there is now concern that if anticipated reductions in concentrations are not achieved in the 11–12 year time frame at the distal end of the plume compliance point, there is not sufficient time to make adjustments to achieve goals within 20 years. In addition, given the plume response to the source treatment, diffusion of contaminants from low-permeability zones may make achieving goals at the compliance point. Options in response to the monitoring information include the following:

• **Reevaluate the CSM** to determine the potential mass storage in the on- and off-site lowpermeability zones. The apparent assumption from Section B.3 ("The concentrations in the remaining compartments were based on anticipated partitioning among the four phases [arrows] and between the transmissive and low-permeability zones per the processes described in Chapter 2. Unfortunately, as is typical of many sites, no data were available from low-permeability zones.") is inaccurate. Additional data collection and refinement of the CSM are required to assess mass storage in the low-permeability zones in the on- and off-site plumes.

• Reevaluate objectives

• A reevaluation of the original objective indicates that this objective is not realistic given that the interim goal was to observe a contaminant reduction trend within 2 years but the measurement point is located 11–12 years travel time away from the treatment area. Therefore, either an interim monitoring well should be placed within 2-year travel time of the treatment location or treatment should be conducted at a point of the plume that is within 2 years' travel from the compliance point.

- Based on the reassessment of mass storage, the time frame for Functional Objective # 1 should be reassessed. A time frame beyond 20 years requires reconsideration of the technologies applied in the plume, preferably the distal end of the plume, should be treated to protect the drinking water well and achieve compliance.
- **Reevaluate technologies**—Table B-5 compares the predicted and actual performance of the remedial technologies to date. Although the PRB has effectively stopped contaminant mass flux from the source to the off-site plume, back-diffusion of contaminants from low-permeability zones may (a) extend the time that contaminant flux discharges from upgradient of the PRB and (b) mask the positive effect in the downgradient contaminant plume for some period of time at compliance wells. Given both of these considerations, the PRB may need to be operated for much longer than planned. Given the limited effect of the PRB on contaminants in low-permeability zone, an evaluation of technologies for contaminants in low-permeability media could be conducted to establish contingent actions should data indicate that the remedy will not meet objectives.

In this example, the functional objectives still appear to be achievable and the existing technologies appear to be performing as designed, but the time frame for treatment may need to be extended due to residual contaminants in low-permeability media. Contingency planning should be conducted to identify alternative courses of action that could be taken to achieve objectives within the desired time frame.

Zonol		Sourc	e zone		On-site plume			Off-site plume				
ZUIIE/	Low permeability		bility Transmissive Low permeability Transmissive		Transmissive		Low perm	eability	Transmi	issive		
pliase	Predicted	Actual	Predicted	Actual	Predicted	Actual	Predicted	Actual	Predicted	Actual	Predicted	Actual
Vapor	2	NA	2	1	NA	NA	NA	NA	NA	NA	NA	NA
DNAPL	2	1	2	1	NA	NA	NA	NA	NA	NA	NA	NA
Aqueous	2	2	2	2	0	0	1	1	0	0	1	0
Sorbed	2	2	2	2	0	0	1	1	0	0	1	0
Concentrat	tion in aqueo	us-phase	equivalents									
0 - no imp	$a_{a} = 1$	On of ug/	2 - 10	o of ug/l	2 - 1000	of ug/l	4 - 1000c	sf u a/l				

Table B-5. Technology performance evaluation matrix

0 = no impact $1 = 1.0s of \mu g/L$ $2 = 10s of \mu g/L$ $3 = 100s of \mu g/L$ $4 = 1000s of \mu g/L$

Appendix C

Conceptual Site Model Checklist

CONCEPTUAL SITE MODEL CHECKLIST

CSM requirement	Status	Required action
Facility		· •
Identify current and historical structures (e.g.,		
buildings, drain systems, sewer systems, underground		
utilities)		
Identify process areas, including historical processing		
areas (e.g., loading/unloading, storage, manufacturing)		
Identify current and historical waste management areas		
and activities		
Other		
Land use and exposure		
Identify specific land uses on the facility and adjacent		
properties		
Identify beneficial resources (e.g., groundwater		
classification, wetlands, natural resources)		
Identify resource use locations (e.g., water supply		
wells, surface water intakes)		
Identify subpopulation types and locations (e.g.,		
schools, hospitals, day care centers)		
Identify applicable exposure scenarios (e.g.,		
residential, industrial, recreational, farming)		
Identify applicable exposure pathways (e.g.,		
contaminant sources, releases, migration, mechanisms,		
exposure media, exposure, routes, receptors)		
Other		
Physical features		1
Identify topographical features (e.g., hills, gradients,		
surface vegetation, or pavement)		
Identify surface water features (e.g., routes of drainage		
ditches, links to water bodies)		
Identify surface geology (e.g., soil types, soil		
parameters, outcrops, faulting)		
Identify subsurface geology (e.g., stratigraphy,		
continuity, connectivity, hydraulic conductivity)		
Identify hydrogeology (e.g., water-bearing zones,		
hydrologic parameters, impermeable strata, direction		
of groundwater flow, preferential flow paths)		
Identify existing soil boring and monitoring well logs		
and locations		
Other		

CSM requirement	Status	Required action
Release information		
Identify potential sources of releases		
Identify potential COCs associated with each potential		
release		
Identify confirmed source locations		
Identify confirmed release locations		
Identify existing delineation of release areas		
Identify distribution and magnitude of COPCs and		
COCs		
Identify migration routes and mechanisms		
Identify fate and transport modeling results		
Other		
Risk management		-
Summarize the risks		
Identify impact of risk management activities on		
release and exposure characteristics		
Identify performance monitoring locations and media		
Identify contingencies in the event performance		
monitoring criteria are exceeded		
Other		
Cleanup		
Identify study options		
Identify study requirements		
Identify cleanup options		
Identify cleanup requirements		
Other		

Appendix D

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Appendix E

Acronyms, Abbreviations, and Symbols

ACRONYMS, ABBREVIATIONS, AND SYMBOLS

A-D	advection-dispersion
AFCEE	Air Force Center for Engineering and the Environment
AMA	American Management Association
bgs	below ground surface
cDCE	cis-1,2-dichloroethene
CERCLA	Comprehensive Environmental Resource, Conservation, and Liability Act
CFR	Code of Federal Regulations
COC	contaminant of concern
CSM	conceptual site model
CVOC	chlorinated volatile organic compound
DCE	dichloroethene
DNAPL	dense, nonaqueous-phase liquid
DOD	U.S. Department of Defense
ECOS	Environmental Council of the States
EGDY	East Gate Disposal Yard
Eh	common measurement of oxidation-reduction (redox) potential
EISB	enhanced in situ bioremediation
ERH	electrical resistance heating
ERIS	Environmental Research Institute of the States
ESB	Engineering Support Building
ESTCP	Environmental Security Technology Certification Program
GETS	groundwater extraction and treatment system
HHE	human health and the environment
IDSS	integrated DNAPL site strategy
IFT	interfacial tension
INEEL	Idaho National Engineering and Environmental Laboratory
ISB	in situ bioremediation
ISCO	in situ chemical oxidation
ISCR	in situ chemical reduction
ITRC	Interstate Technology & Regulatory Council
Κ	hydraulic conductivity
LC-34	Launch Complex 34
LNAPL	light, nonaqueous-phase liquid
MAROS	Monitoring and Remediation Optimization System
MCL	maximum contaminant level
MNA	monitored natural attenuation
MPE	multiphase extraction
NAPL	nonaqueous-phase liquid
NPL	National Priorities List
O&M	operation and maintenance
OoM	order of magnitude
OU	operable unit
P&T	pump and treat

PAH	polycyclic aromatic hydrocarbon
PCE	perchloroethene (tetrachloroethene)
PRB	permeable reactive barrier
RAO	remedial action objective
RCRA	Resource Conservation and Recovery Act
RI	Remedial Investigation
ROD	record of decision
S/S	solidification/stabilization
SMART	specific, measureable, attainable, relevant, time-bound
SVE	soil vapor extraction
SVOC	semivolatile organic compound
TAN	Test Area North
TCE	trichloroethene
TCH	thermal conduction heating
USEPA	U. S. Environmental Protection Agency
VC	vinyl chloride
VOC	volatile organic compound
ZVI	zero-valent iron