Technical/Regulatory Guidance

Optimizing Injection Strategies and In Situ Remediation Performance

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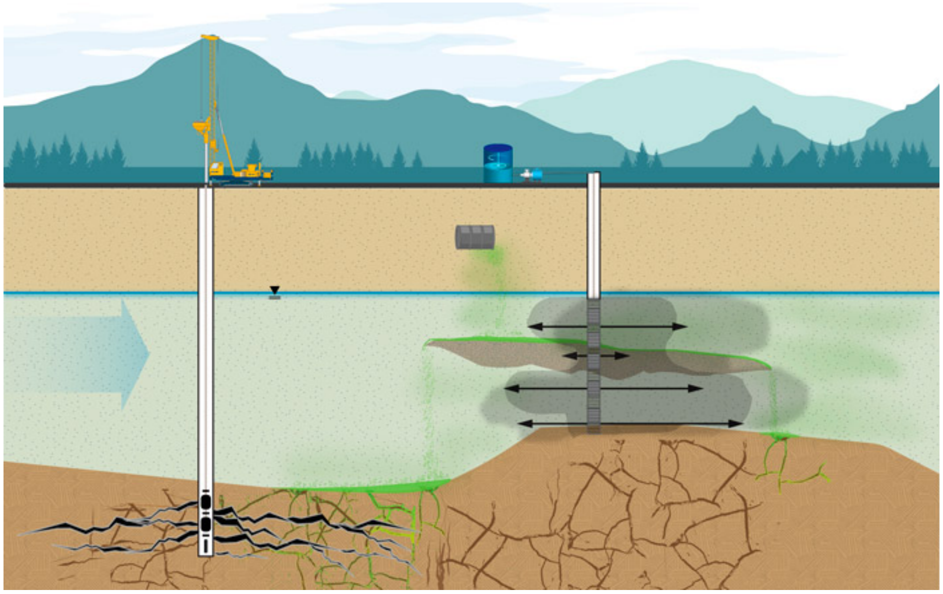

February 2020

Prepared by

The Interstate Technology & Regulatory Council (ITRC)

Optimizing Injection Strategies and In Situ Remediation Performance Team

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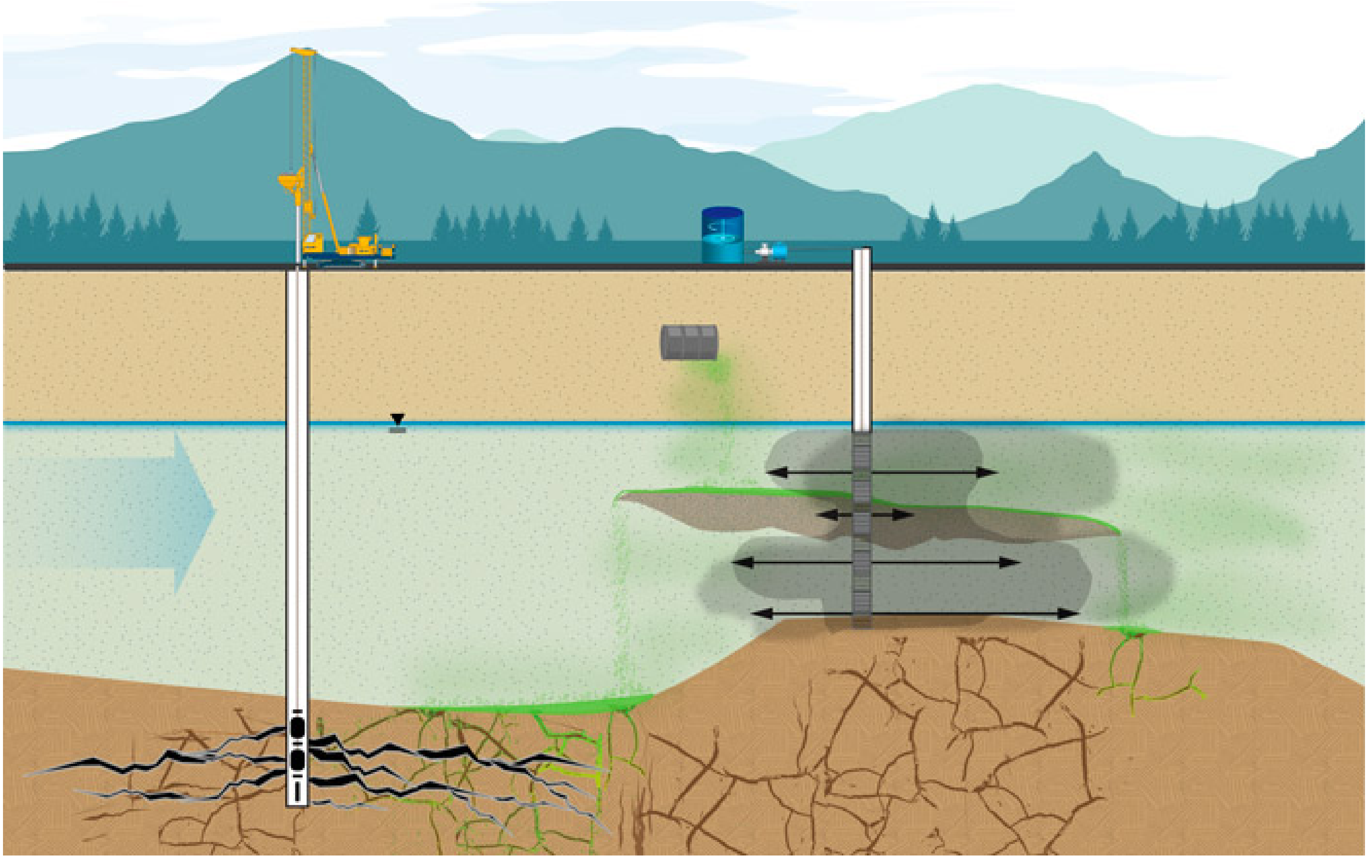

In situ remedies using amendments delivered to the subsurface can be effective, challenges with their implementation can lead to technologies failing to achieve performance or remedial objectives. The Optimizing Injection Strategies and In Situ Remediation Performance (OIS-ISP-1) guidance describes how treatment ineffectiveness can be avoided through effective upfront characterization and design. Additionally, in-progress enhancements to both delivery technologies and amendments can improve performance. Each in situ remedial action requires collection, analysis, and evaluation of the treatment technology, site-specific subsurface characteristics, and groundwater chemical properties to develop an adequate remedial design-level conceptual site model.

There are many types of in situ remediation amendments and emplacement technologies, and each site provides unique challenges that can limit the effectiveness of the in situ remedy. The importance of proactive planning, including using processes such as site characterization analysis, bench- and field-testing and/or design optimization testing, and performance evaluation, cannot be overemphasized. Many challenges encountered during in situ remediation can be overcome with a thorough understanding of the contaminant phase and distribution, site hydrogeology and biogeochemistry, and the amendment's physical and chemical characteristics. All technologies have limitations, and limitations can be addressed, sometimes through combining or sequencing two or more treatment technologies, potentially including alternative or supplemental remedies, or monitored natural attenuation.

This guidance provides the state of the practice based on firsthand knowledge and experiences for a broad audience, including environmental consultants, responsible parties, federal and state regulators, and community and tribal stakeholders.

This guidance includes:

- Remedial Design Characterization, which discusses data required to refine the CSM, remedial design, and implementation plan.
- Amendment, Dose, and Delivery Design, which discusses the iterative and cyclical process of a remedial design.
- Implementation, Monitoring, and Interpretation, which discusses assessment of remedial performance, refinement of the design, and implementation.
- Regulatory Perspectives, which discusses statutory and regulatory challenges and how to address them to improve the chance of success.
- Community and Tribal Stakeholder Considerations, which discusses how to engage with stakeholders before, during, and after a project.

This guidance also includes additional information on the following topics:

- Amendments and Other Additives
- Commonly Encountered Issues Associated with Remedial Design Characterization
- Characterization Parameters for In situ Treatment Remedies
- Injection Fact Sheets
- Case Studies
- Performance Evaluation and Optimization of In situ Remediation Using Amendment Delivery

If you are visiting this site for the first time please review the Introduction of this guidance. All users may find Navigating this Website helpful.

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1 Introduction

In situ treatment (remediation), as discussed in this document, is the delivery and dosing of amendments to enhance the abiotic and biotic processes in the subsurface to treat contaminants in the geologic matrix and groundwater. In situ treatment strategies, tactics, and technologies can be applied to create economically and environmentally sound solutions for remediating subsurface settings impacted by a wide range of organic and inorganic compounds, radionuclides, and other compounds. More than 30 years of experience with in situ treatment has greatly improved the state of the science and engineering, resulting in successful mitigation of contaminants in the subsurface at many sites worldwide. In situ technologies can provide cost-effective methods of treating contaminants with minimal impact to the immediate region and ecosystem (ESTCP 2016).

The general categories of in situ treatments to consider include physical treatment (for example, soil flushing), and/or chemical treatment (for example, chemical oxidation or reduction, surfactant flushing), and biological treatment (for example, enhanced bioremediation, anaerobic dechlorination, bioventing).

Chemical and biological treatment technologies are effective when the amendment is successfully injected in contact with the contaminant mass. Failure to adequately characterize the site and accounting for contaminant mass storage (ITRC 2015, 2018) in low permeability zones are the leading causes of ineffectiveness of these remedy technologies. The spatial distribution of contaminant mass must be fully characterized to the extent needed to design an effective in situ remedy. Although numerous technologies can be applied in situ to treat subsurface contamination, the focus of this document is on technologies where biological and/or chemical amendments are distributed in the subsurface to treat targeted contaminant mass and in some cases modify the geochemical conditions to support such in situ treatment. Contaminant mass includes aqueous or solid forms of contaminants in porous media, fractured rock, or stored in low permeability strata. Storage areas contribute contaminants through back-diffusion from areas with low permeability, porous flow, and fracture flow.

Any in situ technology that involves injection into the subsurface has implementation issues (Appendix B). Treatment ineffectiveness can be avoided through effective up-front characterization and design, and in-progress enhancements to both delivery technologies and amendments can improve performance. Each in situ remedial action requires collection, analysis, and evaluation of the treatment technology, site-specific subsurface characteristics, and groundwater chemical properties, to develop an adequate remedial design-level conceptual site model (Remedial Design Characterization or RDC). This is the first step toward site-specific optimization of the selection of amendments, delivery technologies, and dosing requirements.

In addition to the technical considerations discussed, an initial evaluation of the regulatory requirements must be conducted early in the process. Before spending significant time conducting remedial design investigations, designing injection strategies, or planning a monitoring program, determine the levels of regulatory flexibility and community and tribal support. The design team must ensure that field changes during implementation will be acceptable to the regulators.

1.1 The Problem and the Need for Optimization

Optimization is a foundational part of in situ remediation. Although in situ remedies can be effective, challenges with their implementation can lead to technologies failing to achieve performance or remedial objectives (Alleman 2018). There are many types of in situ remediation amendments and injection technologies, and each site provides unique challenges that can limit the effectiveness of the in situ remedy. This guidance identifies challenges that may impede or limit remedy effectiveness and discusses the potential optimization strategies and specific actions that can be pursued to improve the performance of in situ remediation. The best

A survey by the ITRC team showed that practitioners and regulators see about the same number of in situ proposals; the regulators were approximately 40% more likely to deem the first submittal incomplete. Incompleteness included inadequate information, inadequate CSM, inadequate amendment placement according to the CSM, and a proposed remedy not fully supported by the CSM. For more survey information go to Section 5.2.2.2.

use for this guidance is not to decide whether a particular remedy is the best remedial approach for a particular site. Rather it provides a pathway and instructions to assist the user in identifying either how to design an optimal but not yet implemented in situ remedy, or optimize an ongoing underperforming in situ remedy. This guidance focuses on amendments listed in Table 3-2 and delivery technologies included in the Injection Screening Matrix. The importance of proactive planning, including using processes such as site characterization analysis, Environmental Sequence Stratigraphy (USEPA 2017a), bench- and field-testing and/or design optimization testing and performance evaluation, cannot be overemphasized.

Throughout the text links are included to helpful case studies from team members and other resources

Many challenges encountered during in situ remediation can be overcome with a thorough understanding of the contaminant phase and distribution, site hydrogeology and biogeochemistry, and the amendment’s physical and chemical characteristics. Issues commonly encountered with underperforming remedies are summarized in Appendix B. These issues or common problems are based on field experiences and lessons learned by members of the authoring ITRC team (Appendix H). This Appendix may be used in the planning stage to help identify potential risks, as a guide for managing expectations, or as a resource for optimizing in situ remediation projects. All technologies have limitations, and limitations can be addressed, sometimes through combining or sequencing two or more treatment technologies, potentially including alternative or supplemental remedies, or monitored natural attenuation. E.11, Eastern Surplus Company Superfund Site, Southern Plume Case Study.

Why do initial attempts at implementing in situ remediation often fail or indicate performance below expectations? We can improve the predictability of a positive outcome by:

- understanding common reasons for failures, lessons learned, and best practices Appendix B
- understanding the sequence stratigraphy and depositional environments to adequately map the subsurface in three dimensions
- setting realistic expectations for performance objectives, accounting for uncertainty in CSM and technology limitations (ITRC 2011c; NJDEP 2017)
- considering the long-term value of investigation in regard to life cycle costs (see Section 2.1)
- ensuring the CSM is sufficiently robust for appropriate remedy selection (see Section 2.2)
- selecting appropriate delivery technology to ensure focused delivery of the injectates to have the maximum intended results in reaching the areas of contamination to provide adequate contact, time, and effectiveness
- completing RDC to provide sufficient level of detail for design and implementation (see Section 2.3)
- using adaptive management tools and contingency plans to account for uncertainty (see Superfund Task Force Recommendation #3: Broaden the Use of Adaptive Management, July 3, 2018)
- identifying key decision points and circular feedback loops when performance is not achieving objectives (see Section 3.1)
- managing risk and uncertainty through better characterization (see Section 2.2, & 4.4)
- ensuring that bench and pilot studies are done to verify the efficacy of the proposed remedial alternative during development of the Remedial Investigation/Feasibility Study (RI/FS. see Section 3.3.2)
- interpreting performance monitoring data in a timely manner (see Section 4.4.2)

- optimizing an underperforming in situ remedy (see Section 4.5)
- identifying and understanding potential preferential pathways of injection material

1.2 Intended Audience

This document is designed to provide guidance to those who may not have a comprehensive understanding of the investigation and testing processes involved in optimization of an in situ treatment technique, though many practitioners with limited experience with such technologies will benefit from the overall approach/process to select, implement, and optimize in situ methods. However, the user is assumed to have basic foundational experience with in situ remediation, environmental remediation processes, and natural sciences. This guidance document provides the state of the practice based on firsthand knowledge and experiences for a broad audience, including a variety of government and industry personnel.

Environmental Consultants

▼*Read more*

Consultants have a responsibility to provide options and recommendations for remedial approaches that meet the regulatory requirements and the responsible parties' needs. The technical background of the consultant may not include extensive experience with in situ remedial treatment technologies. This document provides an overview of the currently available technologies and emphasizes the importance of the CSM in the decision and design process.

Responsible Parties

▼*Read more*

Responsible parties may not be familiar with the techniques and current practices for in situ remediation. They may have concerns regarding the costs for detailed, but necessary, site characterization and pilot testing. This document provides information to support in situ remedies while stressing that considering optimization measures in the investigation phase could reduce the schedule and costs over the project's life cycle, when compared to limited characterization that results in partial remediation that ultimately requires additional sampling and analysis, remedial design, and implementation.

Federal and State Regulators

▼*Read more*

Regulators are obligated to verify that the performance of in situ remedial and operational processes are protective. Some of the issues identified are included in Section 5, Regulatory Perspectives. Check with applicable regulatory agencies for any restrictions applicable to injection of materials into the vadose zone that may adversely impact groundwater quality.

Community and Tribal Stakeholders

▼*Read more*

It is very important to perform community outreach early and to inform community and tribal stakeholders of the process and the progress at sites. The local community should be provided opportunities to give input and to understand the planned optimization approach and its potential impact on the surrounding environment and/or cultural values.

1.3 Approaches to Optimizing an In Situ Remedy

The optimization process begins with a refined CSM that conveys a detailed understanding of site conditions and physical limitations necessary to design and install an in situ remedy. Once the geology, hydrology, aqueous geochemistry, groundwater biogeochemistry, and spatial distribution of contaminant mass are understood, amendment screening and selection, dosing, delivery technologies, and performance metrics can be developed.

This document provides guidance for optimizing in situ remediation by:

- refining and evaluating remedial design site characterization data
- selecting the correct amendment
- choosing delivery methods for site-specific conditions
- creating design specifications
- conducting performance evaluations
- optimizing underperforming in situ remedies

As pointed out in the executive summary page iii of an earlier ITRC project (ITRC 2007) *Improving Environmental Site Remediation Through Performance-based Environmental Management*, "As the various environmental cleanup statutes and their implementing regulations evolved, the initial assumption was that these programs could follow a basic *study, design, build* linear paradigm. However, years of experience have led to the realization that the significant uncertainty inherent in environmental cleanup requires more flexible, iterative approaches that manage uncertainty. Uncertainty, as demonstrated by frequently missed target dates, has forced the development of mechanisms that allow for both the systematic reevaluation of initial objectives and the continuous improvement and optimization of remediation technologies and techniques" (ITRC 2007).

This guidance does *not re-create* an entire characterization and remediation process, but relies on the framework described in an earlier ITRC document, titled *Integrated DNAPL Site Strategy* (IDSS) (ITRC 2011c). The IDSS framework is depicted in the left half of Figure 1-1 below. The right half of the figure illustrates the optimization process used in this guidance. Although the decision process has traditionally been viewed as linear, the design of an in situ remedy, in practice, is iterative and cyclical (Superfund Task Force Recommendation #3: Broaden the Use of Adaptive Management, July 3, 2018) with many feedback loops.

Figure 1-1 illustrates that the optimization process for in situ treatment begins with the reevaluation of existing site data to support the selection and design of an in situ remedy. Each of the steps depicted is separately discussed in Sections 2, 3, and 4 of this document. The red icon links to Section 2: Remedial Design Characterization (RDC), which discusses data required to refine the CSM, remedial design, and implementation plan. The data collected and evaluated during RDC activities determine the type of amendment, the amendment dose, and the delivery method represented by the circular green icon. As indicated by the two-way arrow, determination of amendment, delivery, and dose discussed in Section 3 typically occurs as an iterative process, which can include additional site characterization, together with laboratory and/or field pilot testing prior to full-scale implementation. Section 4: Implementation and Feedback (MONITORING) Optimization the blue icon, includes assessment of remedial performance, refinement of the design, and implementation. Optimization as discussed in each of the sections of this document can occur at any of these steps.

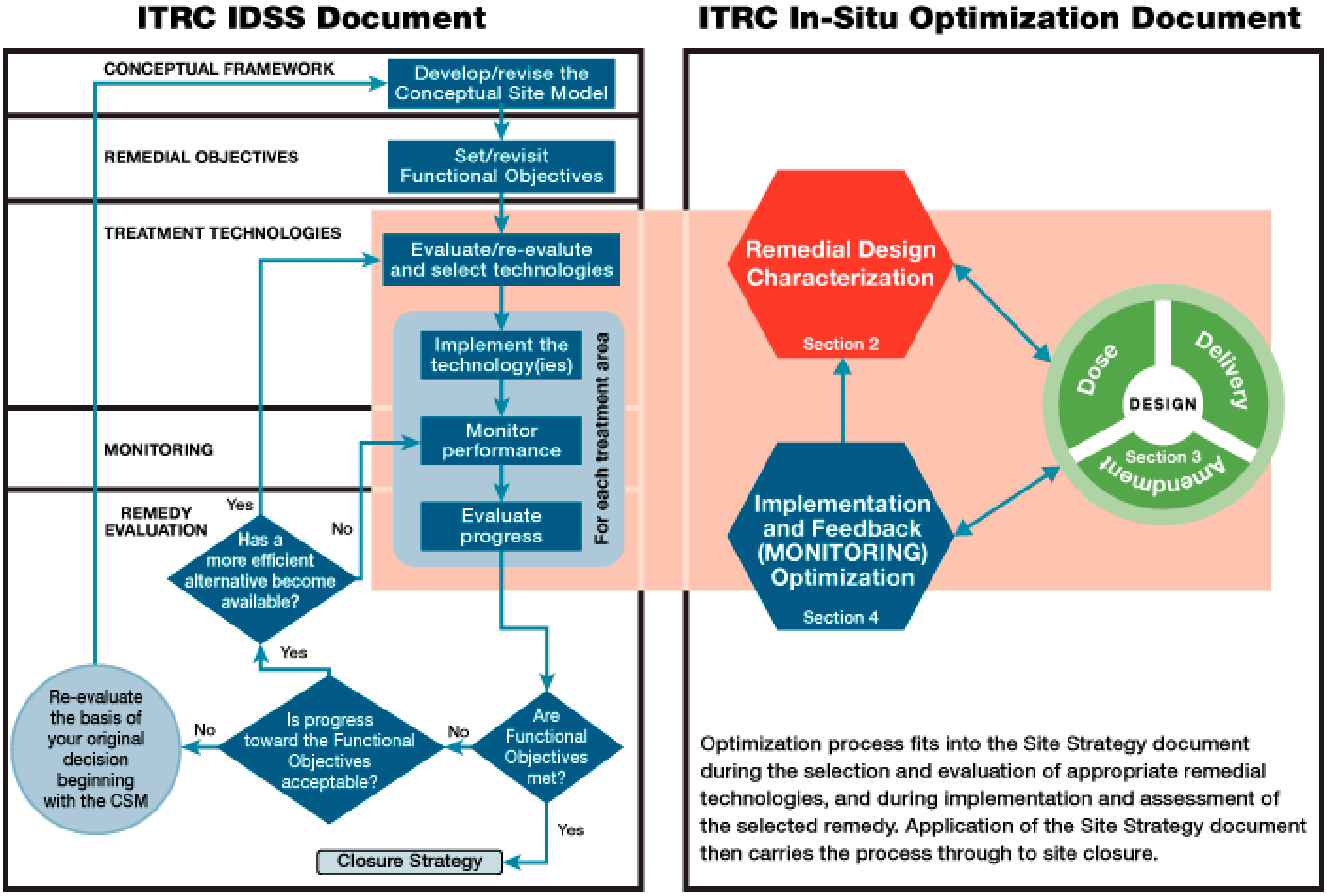

Figure 1-1. The in situ remediation optimization process.

The optimization process fits into the IDSS process during the selection and evaluation of appropriate remedial technologies, and during implementation and assessment of the selected remedy. Application of the IDSS Framework then carries the process through to site closure.

1.4 Document Organization

As described earlier, this document provides guidance to help a remediation professional evaluate site characteristics with in situ treatment in mind. The early investment in detailed data collection, specific to optimize the design of an in situ remedy, reduces the uncertainty of the remedial outcome by promoting an original design that is more effective and improving the chances of successful optimization. Iterative testing and refinement of the amendment composition, dosing, and distribution, even during full-scale implementation, will help ensure that the treatment expectations are met. The following briefly introduces the sections of this guidance.

1.4.1 Section 2 Remedial Design Characterization

▼*Read more*

The RDC section defines additional site characterization data that should be collected, above and beyond what is typically gathered as part of general site characterization studies.

1.4.2 Section 3 Amendment, Dose, and Delivery Design

▼*Read more*

This section provides information on the selection of amendments, delivery methods, and amendment dose. The remedial design process is commonly visualized as a linear sequence that begins with the CSM. However, in practice, the overall process is iterative and cyclical, with many feedback loops at any step connecting to both earlier and later steps.

1.4.3 Section 4 Implementation and Feedback (Monitoring) Optimization

▼*Read more*

Remedy implementation is an iterative process that unites consideration of site characteristics, amendments, and delivery method. This section addresses site-specific logistical and permitting issues that should be considered before mobilizing to the site, as well as during implementation of the remedy, to include changes to dose, amendment, and delivery. The remedy may be optimized at any stage based on the evaluation of monitoring data.

1.4.4 Section 5 Regulatory Perspectives

▼*Read more*

The objective of this section is to identify both statutory and procedural challenges that may impede successful implementation of in situ remedies.

1.4.5 Section 6 Community and Tribal Stakeholder Considerations

▼*Read more*

Given the financial, technical, and regulatory complexities inherent in the in situ remediation process, it is recommended that affected stakeholders should have input to all phases of project decision-making, and that input should continue during the optimization process. If stakeholders are given the opportunity to have meaningful and substantial participation in the decision-making process, they are more likely to support changes in technical approaches. In addition, positive interaction through quality community involvement programs fosters respect among community members and project decision makers, one of the foremost factors determining whether communities accept project remedies.

2 Remedial Design Characterization

RDC refers to gathering of additional data, beyond general site characterization studies, necessary to develop a sufficiently detailed CSM to enable design basis for an in situ remedy. When in situ remedies fail or are less effective, it is often due to a lack of detailed understanding and an insufficiently developed CSM leading to poor design and implementation. The success of in situ remedies is directly related to a thorough understanding of site and subsurface conditions.

The RDC comprises the data required to obtain a focused understanding of the geologic, hydrogeologic, microbial, and geochemical nature of the site conditions in specific support of in situ remedial actions. The purpose of this section is to discuss these parameters as they affect in situ remediation approaches, design, and implementation.

2.1 Cost Benefits of RDC

2.1.1 Value of Investigation

The RDC will describe the data required to gain a focused understanding of the geology, hydrogeology, microbial, and geochemical nature of the site conditions in specific support of in situ remedial actions. These additional data can be used as part of the final remedy design discussed in Section 3, and have been shown to provide a value of investigation (VOI) by contributing to a successful design and implementation.

Remediation practitioners must evaluate the benefits of investigation costs against the value of the outcome. This idea of *return on investigation*, discussed in ITRC's *Integrated DNAPL Site Characterization and Tools Selection* (ITRC 2015), referred to here as VOI, also applies in the context of the RDC. Performing an RDC will incur upfront costs beyond those for a general site characterization; however, it can be expected to result in a more successful remedial design and implementation.

Following initial site characterization, typical historical practice was to move immediately to the remedy selection and design phase, to demonstrate remedial progress quickly. This required generalizations and assumptions to be made about subsurface geology, contaminant distribution, and geochemistry. Experience over the past several decades has shown that this historical practice often leads to poor quality outcomes, repeat treatments, or in some cases, selection of a different, more appropriate remedy altogether. RDC, however, allows for a more accurate, design-level characterization, and consequently, a more effective remedial strategy, shorter remedial time frame as significant rework is not required, and lower costs over the project life cycle. This is shown conceptually in Figure 2-1, and a case study is presented in Section 2.1.2.

Special precaution: Preferential pathways and heterogeneities, whether manmade or natural, may affect groundwater flow. It is critical to have a comprehensive understanding of the subsurface stratigraphy to reduce the likelihood of a flawed CSM. (USEPA 2017b; ITRC 2011c; NAVFAC 2013b) presents six case studies of various stratigraphic characteristics that demonstrate the importance of understanding the subsurface to optimize design, and one case action demonstrating remediation cost savings following design changes.

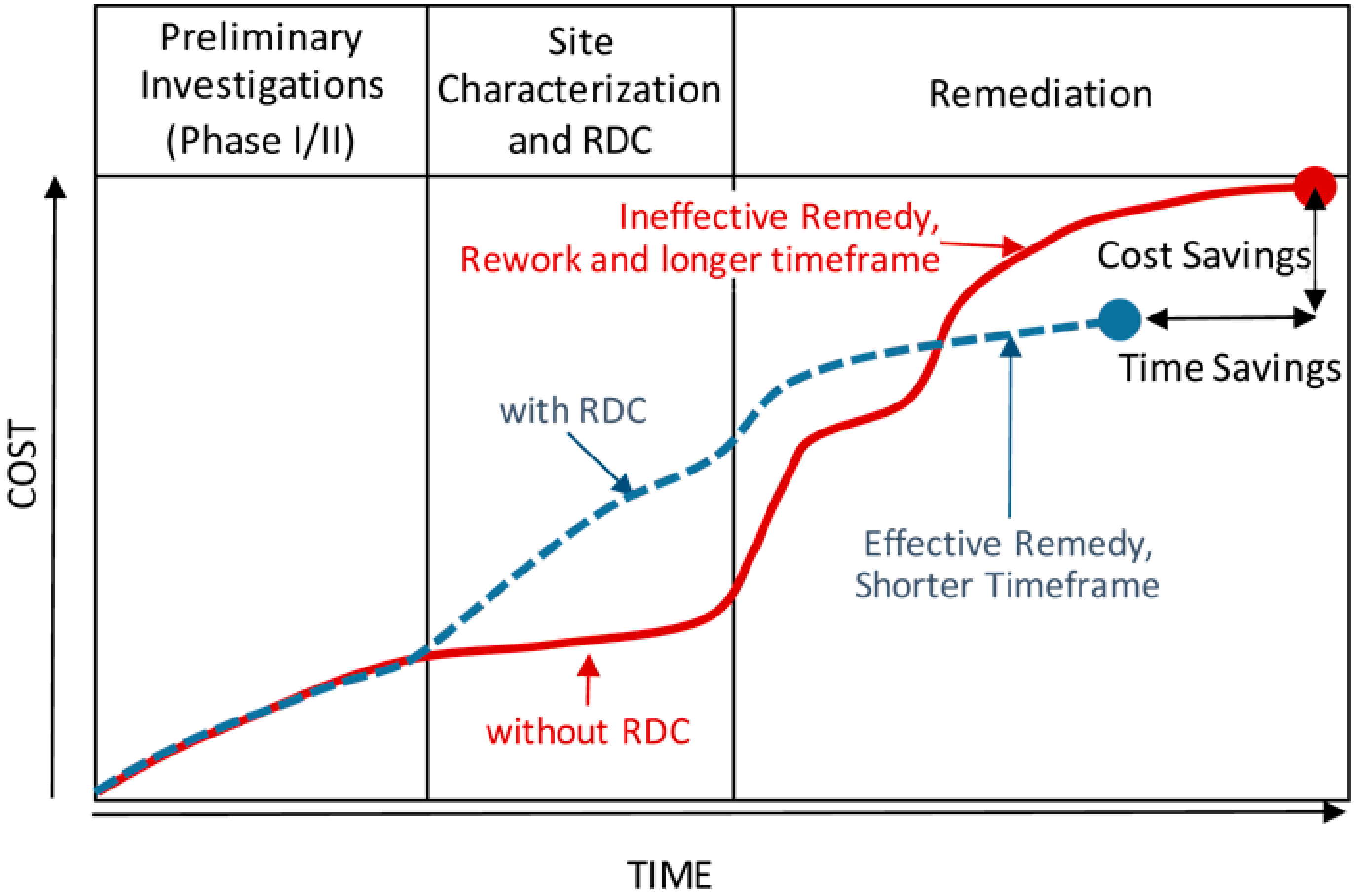

Figure 2-1. Conceptual project lifecycle costs with and without RDC.
Source: Modified from (ITRC 2015)

2.1.2 VOI Case Study

The VOI concept is well illustrated by the following project example. Soils and groundwater were impacted at an approximately 20-acre site. The geology was characterized as floodplain deposits with the target saturated zone occurring as a few-foot-thick sand lens approximately 15 feet below grade, confined within thick, hard clays above and below.

Under a tight time frame to remediate the downgradient portion of the site and plume in preparation for redevelopment, an enhanced in situ bioremediation (EISB) program was quickly implemented, using sodium lactate as the carbon source to address chlorinated aliphatic hydrocarbon contaminants. Though the geology was fairly well characterized and the injections were properly performed within the sand interval, the following RDC steps had not been implemented:

- Site-specific hydraulic conductivity was not evaluated, nor was an injection test performed to estimate the radius of influence (ROI); thus, the ROIs of the individual injections did not overlap.
- Geochemical parameters were measured, but these were not used to assess the viability of EISB at the site.
- Neither laboratory-scale nor field pilot-scale treatability testing was performed; rather, the choice of substrate and the dosing was based on data from similar sites.
- Microbial studies had not been performed to assess whether the microbial community comprised appropriate and sufficient bacteria.

Moreover, the upgradient source(s) were not addressed prior to implementation of remediation in the downgradient portion of the plume, allowing recontamination to potentially occur.

During monitoring that occurred over 2 years following the EISB program, no reductions in groundwater contamination concentrations occurred, and the geochemical properties of the aquifer at the monitoring locations were unchanged. Due to this remedy failure, site redevelopment was delayed. The site had to be recharacterized, including better definition of source areas, better plume definition, more strategically placed monitoring wells, aquifer testing to more closely estimate hydraulic conductivity and (pumping) ROI, microbial testing, and treatability studies to assess various substrates and specify dosing. In addition, the newly delineated source soils were removed. In the end, due to relatively low concentrations following source removal and low risk of back-diffusion/rebound, it was decided that the most effective remedy for the site was groundwater extraction, focusing on the source area and allowing for monitored natural attenuation in the downgradient areas.

The cost and time impacts of the project are summarized in Table 2-1. The cost of remedy failure without RDC was $380,000 and three years of delay. Had RDC been performed at the outset, the EISB program would never have been implemented, which would also have saved three years of project time. These cost and time impacts do not consider– the opportunity cost lost to the owner due to delay of site redevelopment.

Table 2-1. VOI Case Study—Cost and Time

	Item	**Costs**		**Years**	
		VOI Case Study	Hypothetical Using RDC	VOI Case Study	Hypothetical Using RDC
	Initial Site Characterization	$150,000	$150,000	2	2
	Upfront RDC (Hypothetical)	$0	$160,000	0	1
Failed Remedy	EISB Implementation	$300,000	$0	1	0
	EISB Monitoring	$80,000	$0	1	0
Rework (RDC & Remedy)	RDC (as part of rework)	$160,000	$0	1	0
	Remedy Implementation	$200,000	$200,000	1	1
	Monitoring and Closure	$70,000	$70,000	1	1
	Totals	$960,000	$580,000	7	5
	Cost Savings and Time Saved with RDC	**$380,000**		**2**	

2.2 Characterization Parameters for Refining the CSM

Understanding the heterogeneity of the subsurface, its influence on the distribution and transport of contaminants, and the hydrogeochemical fate of dissolved, separate phase, and sorbed contaminants at a level of characterization required for a successful in situ remedy depends on: (1) delineation of lithology/stratigraphy, fracture characteristics, and soil/aquifer properties that define flow characteristics and soil-water-contaminant interactions; (2) geochemistry and mineralogy that identifies, for example, competing electron acceptors or metals mobilization risks; and (3) characterization of the microbial community and other factors that provide a measure of contaminant degradation or immobilization potential.

Table 2-2 provides a comprehensive (but not exhaustive) list of characterization parameters relevant for in situ remediation. The table provides a general guidance on the relevance of these parameters for biotic and abiotic in situ remedies, and the stage at which they should be considered (e.g., during the screening process for selecting the most appropriate amendment and delivery strategy; during remedial design; and/or during implementation and performance monitoring). Parameter definitions and further explanation can be viewed by hovering over the parameter term in the left column of Table 2-2.

Table 2-2. Characterization parameters for in situ treatment remedies

Parameter	**In situ Approach**		**Remediation Phase/Step**		
	Abiotic	**Biotic**	**Alternatives Screening**	**Remedial Design**	**Performance Monitoring**
Physical Properties					
Provenance and Mineralogy	M	M	HIGH	MEDIUM	LOW
Stratigraphy	M	M	MEDIUM	HIGH	LOW

Parameter	**In situ Approach**		**Remediation Phase/Step**		
	Abiotic	**Biotic**	**Alternatives Screening**	**Remedial Design**	**Performance Monitoring**
Degree of Weathering of Geologic Formation	M	M	MEDIUM	HIGH	LOW
Fracture Representative Aperture and Length	M	M	MEDIUM	HIGH	LOW
Fracture Connectivity/Rock Quality Designation	M	M	MEDIUM	HIGH	LOW
Fracture Orientation	M	M	MEDIUM	HIGH	LOW
Grain Size Distribution	M	M	LOW	HIGH	LOW
Bulk Density	M	M	LOW	HIGH	LOW
Fraction of Organic Carbon	M	M	MEDIUM	HIGH	LOW
Primary and Secondary Porosity	M	M	MEDIUM	HIGH	LOW
Flow Properties					
Flow Regime	M	M	HIGH	HIGH	HIGH
Groundwater Occurrence and Variability	M	M	HIGH	HIGH	HIGH
Hydraulic Conductivity	M	M	HIGH	HIGH	LOW
Degree of Heterogeneity	M	M	HIGH	HIGH	LOW
Anisotropic Orientation	M	M	HIGH	HIGH	LOW
Effective Porosity	M	M	HIGH	HIGH	LOW
Velocity/Flux	M	M	HIGH	HIGH	HIGH
Aqueous Geochemistry					
pH	M	M	HIGH	HIGH	HIGH
Temperature	M	M	HIGH	HIGH	HIGH
Alkalinity	M	M	HIGH	HIGH	HIGH
Conductivity, Salinity, and Total Dissolved Solids (TDS)	M	M	MEDIUM	MEDIUM	MEDIUM
Oxidation-Reduction Potential (ORP)	M	M	HIGH	HIGH	HIGH
Dissolved Oxygen (DO)	M	M	HIGH	HIGH	HIGH
Nitrate (NO_3^-)	L	M	HIGH	HIGH	MEDIUM
Nitrite (NO_2^-)	L	M	LOW	LOW	MEDIUM
Manganese Manganic (Mn^{+4})	L	M	LOW	MEDIUM	MEDIUM
Manganese Manganous (Mn^{+2})	L	M	MEDIUM	MEDIUM	MEDIUM
Ferric Iron (Fe^{+3})	M	M	LOW	HIGH	HIGH
Ferrous Iron (Fe^{+2})	M	M	MEDIUM	HIGH	HIGH
Sulfate (SO_4^{2-})	M	M	HIGH	HIGH	HIGH

Parameter	**In situ Approach**		**Remediation Phase/Step**		
	Abiotic	**Biotic**	**Alternatives Screening**	**Remedial Design**	**Performance Monitoring**
Sulfite (SO_3^{2-}), Sulfide (S^{2-})	M	M	LOW	MEDIUM	HIGH
Chloride (Cl^-)	L	M	MEDIUM	LOW	MEDIUM
COD (chemical oxygen demand)	L	L	LOW	LOW	LOW
SOD (soil oxidant demand)	M	L	MEDIUM	HIGH	LOW
TOD (total oxidant demand)	M	L	MEDIUM	HIGH	LOW
NOI (natural oxidant interaction)	M	L	MEDIUM	HIGH	LOW
TOC (total organic carbon)	M	M	MEDIUM	HIGH	MEDIUM
Anions, cations	***Individually listed***				
Arsenite (As^{+3})	M	L	LOW	MEDIUM	HIGH
Arsenate (As^{+5})	M	M	MEDIUM	HIGH	MEDIUM
Chromium (Cr^{+3})	M	M	MEDIUM	HIGH	MEDIUM
Chromium (Cr^{+6})	M	L	LOW	MEDIUM	HIGH
Other Heavy Metals (e.g., lead, copper, selenium)	L	L	LOW	MEDIUM	MEDIUM
Microbiology					
Stable Isotope Probing	L	M	LOW	MEDIUM	MEDIUM
PLFA (Phospholipid Fatty Acids)	L	M	LOW	MEDIUM	MEDIUM
qPCR (Quantitative Polymerase Chain Reaction)	L	M	LOW	MEDIUM	MEDIUM
Degradation Potential					
CSIA (ITRC 2013a) (Compound-Specific Isotope Analysis)	M	M	LOW	MEDIUM	MEDIUM
Dissolved Hydrocarbon Gases (Methane, Ethane, Ethene, Acetylene, Propane, Propene)	M	M	LOW	LOW	MEDIUM
Carbon Dioxide (CO_2)	L	M	LOW	LOW	MEDIUM
Magnetic Susceptibility	M	L	MEDIUM	LOW	LOW
Legend					
More applicable	M				
Less applicable / not applicable	L				
	LOW				
Relative importance of data at the remediation phase indicated	MEDIUM				
	HIGH				

These parameters help refine the CSM at the onset of in situ remediation planning. General guidance for preparing and refining the CSM has been discussed in previous ITRC documents (ITRC 2011c, 2017a). RDC is an effort to refine the CSM prior to the remedial design stage. This refinement begins with a careful review of the existing CSM in context of the in situ treatment options being considered for the site target treatment zone (TTZ, See section 3.2.1) and developing the data collection objectives to fill the data gaps that reduce uncertainties in the design and implementation of the considered in situ remedy (or remedial options). Site parameters that control the amendment delivery in the subsurface, and establishing contact between target contaminants and amendments, are critical to treatment success. Furthermore, higher resolution data, or data density, increases the likelihood of treatment success (Appendix E-3, Rapid Site Closure of a Large Gas Plant Using In situ Bioremediation Technology in Low Permeability Soil and Fractured Rock Case Study).

Through RDC, the CSM will continue to improve and evolve as the site moves from feasibility study to design, remedy implementation, monitoring and evaluation, and subsequent optimization efforts. Furthermore, data collected at each stage of bench study, pilot testing, and full-scale implementation can and should be used to continue to refine the CSM. This philosophy of updating the CSM during each remediation stage is consistent with the *adaptive management* principles discussed in *Characterization and Remediation of Fractured Rocks* (ITRC 2017b); *Integrated DNAPL Site Strategy* (ITRC 2011c); and Superfund Task Force Recommendation #3: Broaden the Use of Adaptive Management, July 3, 2018. This is further discussed in Section 3.1 and depicted in the design wheel of Figure 3-1.

2.3 RDC Considerations

The main considerations of in situ RDC are:

- remedy performance objectives
- site characteristics
- contaminant distribution
- geology and hydrogeology
- geochemistry and microbiology

2.3.1 Remedy Performance Objectives

Remedy performance objectives, or expectations, provide a framework to measure key milestones and associated risk reductions. Although the (ITRC 2011c) discusses the overall remedy performance objectives in detail, the purpose of this section is to describe the characterization needs pertaining to remedy performance objectives for injection-based remedies in particular. Key components of performance objectives specific to these types of remedies include a defined TTZ where the remedy will be implemented, and in what depth intervals, the expectations in terms of observations and outcomes during and after the injections, and time frame for the observations and outcomes of the remedy. These concepts are discussed further below.

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Performance objectives should be established once the TTZ has been defined within an adequate CSM framework. The performance objectives will vary depending on the TTZ, contaminants of concern (COCs) and their physical forms, the amendment type, the method of delivery, and the robustness of the CSM. A highly prescriptive goal, such as achieving a defined reduction in contaminant concentration following injection as the only measure of success, requires an RDC design-related CSM that contains minimal uncertainty. This may not be practical for all sites; therefore, a combination of contaminant reduction objective(s) coupled with other lines of evidence can allow for meaningful data collection to show progress toward defined performance objectives. Examples of different types of performance objectives are presented in Table 2-3.

Table 2-3. Examples of injection-based remedy performance objectives

Example Remedial Performance Absolute (ITRC 2011c) Objective	**Measured by**	**Used for**
Amendment Distribution	Presence of amendment components or reaction products (e.g., specific conductance, pH, total organic carbon, sulfate, oxidant, tracer, etc.) in the treatment zone	Validate reagent(s) was delivered to targeted treatment interval; used to confirm injection volume versus ROI relationship; used to differentiate between amendment consumption and dilution
Reagent Pore Concentration	Groundwater concentration of reagent/amendment post-injection. (Recalcitrant groundwater constituents may act as ad hoc tracers.)	Validate amendment was delivered at working strength (i.e., dose) to the TTZ; used to evaluate dilution of amendment post-injection and rate of wash-out and degradation
Contaminant Concentration Reduction	Concentrations post-injection from individual monitoring wells (not injection wells)	Evaluate effectiveness of the injection within the treatment zone at discrete points. Note that in the short-term this evaluation will require collection of amendment data to determine dilution versus destruction.
Contaminant Mass Flux Reduction	Post-injection change in concentrations within a cross-gradient plane of the treatment zone in a transect oriented perpendicular to groundwater flow	Evaluate reduction of mass flux downgradient of the treatment zone following injection

A method of establishing achievable remediation objectives is described in detail in chapter 3 of *Integrated DNAPL Site Strategy* (ITRC 2011c). The performance objectives summarized in Table 2-3 can complement one another and be used to optimize future injections. As part of the remedy, performance evaluation data should be used to assess the success of the injection while also providing information for optimizing future injection as part of an overall adaptive remedy management approach.

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Remedy performance objectives (section 3.1 in (ITRC 2011c) are typically oriented toward achieving short-term metrics to ensure the project is on track to meet the overall site objectives (see section 3.1, Absolute Objectives (ITRC 2011c). It is recommended that any remedy performance objectives incorporate multiple lines of evidence. This enables an adaptive site management approach for implementation of injection-based remedies, particularly when it comes to meeting stakeholder time frame expectations. The adaptive site management approach is discussed in *Remediation Management of Complex Sites* (ITRC 2017b) and refers to a comprehensive, flexible, and iterative process to manage long-term remediation projects. The adaptive site management approach is applicable to all injection-based remedies to meet both short-term and long-term objectives. Development of remedial performance metrics to track progress toward reaching objectives, and the communication of the development process, metrics, and objectives, will ensure that the injection-based remedy is positioned for success with all stakeholders.

2.3.2 Site Characteristics

In addition to the hydrogeologic and hydrogeochemical characteristics presented in Table 2-2, a first step in the RDC includes planning for general site characteristics, both natural and anthropogenic. For example, to ensure appropriate access for reagent delivery, a sufficient understanding of utility corridors and how they may impact injection point placement is necessary. Additional site characteristic items are discussed in Table 2-4.

Table 2-4. General site characteristics

Accessibility	Definition	Physical, logistical, or legal obstacles to predesign characterization and implementation at the site (e.g., building locations, roads, subsurface utilities and tank systems, high traffic areas, overhead utilities, small property size, vegetation, property security).
	Impact	Site accessibility influences the design and implementation of some technologies more than others, due to equipment size, degree of work space footprint, below-grade utilities, etc. Technologies that require a larger work space footprint may be less feasible to implement. There may also be challenges related to targeting contamination that is located under buildings or roads or within mechanized equipment exclusion zones for utilities, tank systems, etc. Often there is limited ability to characterize these areas and their impact on design and dosing. There are further challenges related to the potential for vapor intrusion into buildings.
Sensitive to Disturbance Areas	Definition	An area with a high likelihood for disturbance or disruption of normal activities (e.g., residences, schools, businesses, wildlife, etc.) due to noise, increased traffic, or physical obstruction.
	Impact	At sites with more potential for disruption such as nearby businesses or residential areas, certain technologies may be less feasible, or additional planning and coordination may be necessary to reduce disruption and ease public concern during disruptive activities such as drilling, piping installation, sampling, or interruption of normal traffic and utility use.
Health and Safety	Definition	Regulations and procedures intended to prevent illness, accident, or injury at work spaces and public environments. Safety considerations apply to field crews, consultants, regulators, and the general public.
	Impact	Site-specific safety considerations may limit the use of certain technologies. Additional planning may be necessary to address special handling and use of certain amendments and to ensure that work crews are specially trained and experienced with the chosen technology. Considerations for site security, fencing, lighting, and traffic control are important early on in the design process.
Utility Availability	Definition	The presence and usability of water supplies, electricity, sewer, and stormwater infrastructure at a site.
	Impact	Some technologies require large amounts of water for injections as well as electricity for equipment. Some technologies may be less feasible in remote areas, or additional planning may be necessary to gain access to these utilities. Coordinating water transport and storage, fuel storage, and waste disposal should be considered during the design process.
Sensitive Receptors	Definition	Any feature that may be adversely affected by hazardous materials, remedy construction, and operations. This would include public drinking water sources; endangered species; protected wetlands, riparian habitats, or other sensitive ecological areas; cultural sites; schools/daycares; and hospitals.
	Impact	Sensitive receptors may impact the design and implementation of some technologies more than others, due to restrictions of equipment size, work space footprint, operation times, and amendment selection, etc.
Current and Future Land Use	Definition	The classification of land according to what activities take place on it or how humans occupy it, including future restrictions on land use and zoning.
	Impact	The proposed design may need to account for current or future infrastructure and potential restrictions due to area zoning. Deed or site usage restrictions may be necessary to prevent potential exposure pathways.

Former Operations	Definition	Detailed understanding of the different operations and processes at a site and the types of chemicals used and stored, along with the locations of these operations and storage areas.
	Impact	Past activities at the site should be taken into consideration to help refine the CSM. For example, not all activities may be related to the contaminant of concern, but may be important when evaluating the potential for mobilization of other compounds (e.g., metals, PFAS) or evaluating preferential pathways due to historical placement of fill or dumping areas.
Buried Infrastructure	Definition	Subsurface features including utilities (water, sewer, electric, communications, natural gas, stormwater, etc.), underground storage tanks, and drainage networks (modern and historic).
	Impact	Reduce chances of damage to buried infrastructure during remedy construction and operation with effective remedy design. Identify features that may facilitate chemical interactions and create conduits for chemical or amendment migration. Buried infrastructure may create pathways for injected material to migrate in undesired areas and for vapors to travel into buildings.

2.3.3 Contaminant Distribution

A detailed, three-dimensional understanding of contaminant distribution (ITRC 2016) is necessary to minimize uncertainty associated with selection and implementation of in situ remedies. Following a typical site characterization, the contaminant plume will generally be delineated areally and a contour map drawn using a widely spaced monitoring well network or grab groundwater data. Such maps are useful to identify higher concentration areas to focus on for remediation, but due to the sparsity of the data, can often overestimate treatment areas. Similarly, vertical discretization of contamination will provide focus on targeted injection intervals, compared to arbitrarily long intervals perceived from monitoring well data. A better approach is to refine areal and vertical contaminant distribution as part of an RDC. The cost benefits of such an RDC are discussed in Section 2.1 and illustrated by a project example in Section 2.1.2.

A detailed, three-dimensional picture of contaminant distribution is also necessary to decide upon the in situ approach, which typically takes one of two forms: (1) focus in situ remediation on high concentration source and hot spot areas, allowing natural processes to attenuate the distal, low-concentration plume; or (2) implement in situ remediation as a long-term, downgradient control mechanism, with tightly spaced injections forming a reactive zone through which contamination is treated as it flows under the natural gradient.

As well, knowledge of the contaminant phases—that is, light nonaqueous phase liquids (LNAPL), dense nonaqueous phase liquids (DNAPL), aqueous, sorbed (in the case of organics), mass and dissolved or precipitated (in the case of metals)—is necessary to identify the most effective in situ strategy, or whether in situ would be effective at all. For example, amendment loading and delivery approaches will be different for separate phase contamination versus aqueous (as will be discussed in Section 3), and in the case of strongly sorbing compounds, neglecting to include the sorbed fraction will result in underestimated amendment dosing. Further, due to back-diffusion from lower permeability matrices, multiple injection events may be needed, which is another design element that must be considered and understood at the outset.

Multiple tools are available to enable high-resolution contaminant characterization and related geologic and hydrogeologic data. Description, use, and implementation strategies are presented in ITRC's *Implementing Advanced Site Characterization Tools* document (ITRC 2019).

2.3.4 Geology and Hydrogeology

The general concept that contaminants migrate via the more advective pathways such as more permeable, coarser-grained sand or highly fractured bedrock, and are stored or sequestered in low permeability, finer-grained matrices is a key aspect for approaching injection-based technology designs. Ultimately, more permeable media, rock, and fractures control the advancement of injection fluids both vertically and laterally from a delivery point. However, the less permeable formations, which limit the injectates to be in contact with the contaminants present in the tighter formations, will eventually determine the success or failure of the in situ remedies. These features play a significant role in the advective and diffusive distribution of amendments following delivery. Although classical hydrogeologic interpretations remain important, a more focused understanding of specific site aquifer flow parameters and contaminant transport is required to ensure that the objectives of the injections are achieved.

Geologic (aquifer physical properties) and hydrogeologic (aquifer and groundwater flow properties) elements important to the RDC are listed in Section 2.2. In addition to these properties, tracer or injection tests can be used as part of an RDC, or during the initial injection event, to develop or validate the key assumptions used in the design. Tracer tests may include an inert tracer (e.g., salts such as bromide, fluorescent dyes, isotopes) or a component of the amendment. Depending on the objectives, the amendment itself may serve as a pseudo tracer. In this case, components of the amendments (e.g., sulfate from a persulfate injection, or purple color from a permanganate injection, total organic carbon (TOC), increased dissolved oxygen (DO), or white color or turbidity from some emulsions) can be used for short-term assessments, such as evaluating the postinjection volume-radius relationships, and immediate dilution of the amendment following injection. As these types of injection tests do not intentionally include an inert tracer, they may not accurately be able to satisfy potential longer data collection needs (that is, groundwater velocity), because the amendment components themselves can be reactive, biodegrade, or sorb to soil matrix surfaces.

Tracer or injection testing ideally should be conducted at the beginning of an injection-based remedy. However, these tests can be performed at any point during an injection program. Data collected as part of a tracer or injection test can be used for several activities, including optimizing the injection program, (see Section 4.4.1) troubleshooting problem areas (see Section 4.5), evaluating the cost benefit of supplemental injection infrastructure, or evaluating use of a different amendment and/or amendment strength. Additional information on design of an appropriate field test (including use of tracers) can be found in Section 3.3.3.

2.3.5 Geochemistry and Microbiology

The geochemical parameters and microbial populations present in a hydrogeologic setting provide critical information that feeds into in situ remediation selection (that is, aerobic or anaerobic biostimulation, chemical oxidation or reduction) and design. They also provide a pre-remediation baseline, which enables the practitioner to evaluate remedy performance. Each geochemical and microbial parameter is discussed in these contexts in Table 2-2.

In situ technologies can be broadly categorized into two types: biotic and abiotic. Abiotic technologies are further differentiated into in situ chemical oxidation (ISCO) and in situ chemical reduction (ISCR, which can also include biotic breakdown), and activated carbon–like sequestration. Chemical remedies will directly destroy (for organics) or modify (for metals) the target contaminant via chemical reactions. Biological remedies enhance or promote microbial reactions to achieve performance goals either by stimulating existing microbes (biostimulation), or by adding specialized microbes (bioaugmentation). The different types of in situ chemical and biological amendments associated with these remedies are discussed in greater detail in Section 3.4 and Amendment fact sheets.

A method to evaluate the current state of an aquifer is to start with a monitored natural attenuation (MNA) assessment. Several existing documents provide great detail on performing an MNA assessment (USEPA 1998; ITRC 2008a), and can be used as a baseline for design of any in situ treatment strategy, or as a basis for screening out a technology. Establishing new processes or changing the current state of an aquifer is possible, but can be difficult, costly, and take a long time to implement. Regardless of the type of remedy (chemical or biological), it is recommended to conduct a baseline rate assessment to define the initial degradation rate prior to injection of an amendment. This will allow for a *before* and *after* evaluation to determine whether the in situ injection–enhanced degradation rates are sufficient to meet performance objectives.

The following sections detail data that can be used to support screening the type of in situ injection technology and associated amendment.

2.3.5.1 Degradation Products and Microbiology

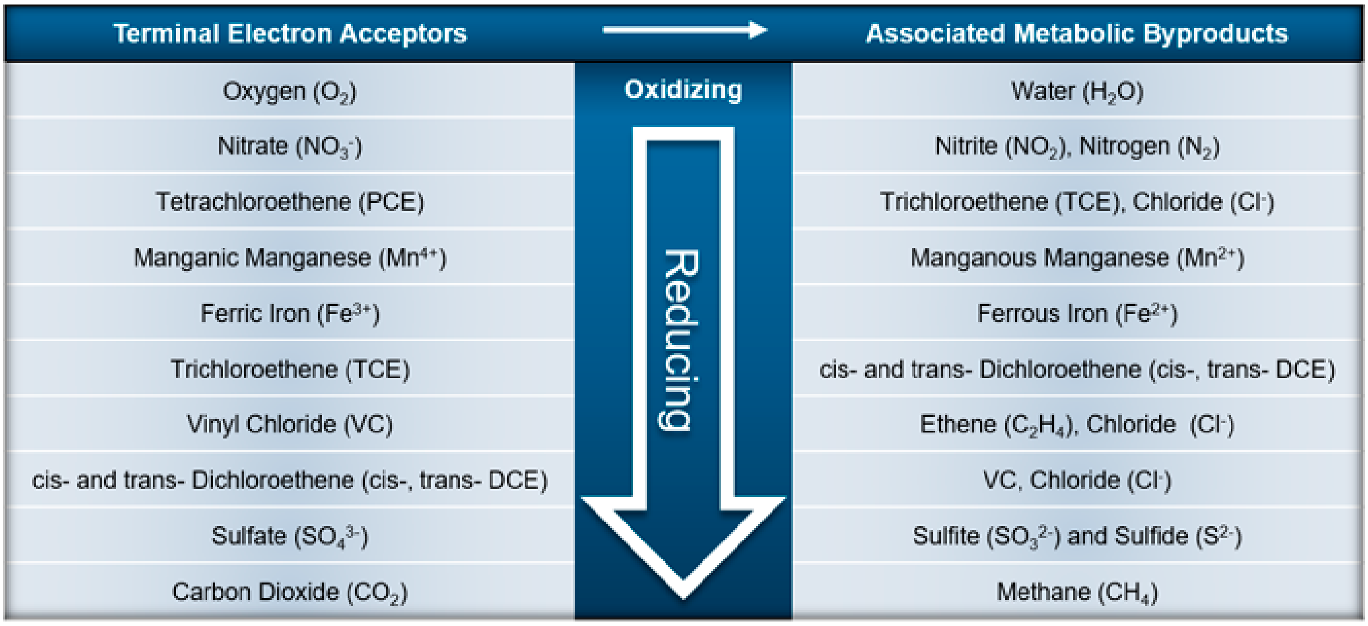
When remedies that include biotic technologies are under consideration, an analysis of biological degradation products (where applicable) should be completed as part of the screening process. For example, light gas data (methane, ethane, ethene, acetylene) should be collected in addition to volatile organic compound (VOC) data (including degradation daughter products) at chlorinated sites to assess whether complete reductive dechlorination by native microbes is already occurring at the site.

Collection of microbial data can be used as another line of evidence for the support of a biological remedy. Several microbial tools are available for use in site assessment (ITRC 2013a), with new technologies frequently brought to market. One of the most commonly used and commercially available tools for pre-assessment is quantitative polymerase chain reaction (qPCR), in which key species or functional genes can be evaluated in soil and/or groundwater. The results of these tests can determine presence/absence and relative abundance of microbes or functional genes prior to biostimulation activities.

Several other tools are also available for microbial testing, with the best tool dependent on the type of information needed to support the assessment (ITRC 2013a).

2.3.5.2 Geochemistry

Collection of baseline geochemistry data is suggested from locations within, and outside of, the contaminant plume. Several locations may be desired for sampling, including within a source area, the dissolved core of the plume, the toe of the plume, and upgradient or side-gradient of the plume (for background information). Geochemical data typically collected during an MNA study are listed and described in Table 2-2. Figure 2-2 shows how the geochemical data can be used to evaluate reducing conditions. As one goes down the table progressively reducing groundwater conditions are indicated. Select contaminants are included for reference.



Terminal Electron Acceptors	→	Associated Metabolic Byproducts
Oxygen (O_2)	Oxidizing	Water (H_2O)
Nitrate (NO_3^-)	Reducing	Nitrite (NO_2), Nitrogen (N_2)
Tetrachloroethene (PCE)		Trichloroethene (TCE), Chloride (Cl^-)
Manganic Manganese (Mn^{4+})		Manganous Manganese (Mn^{2+})
Ferric Iron (Fe^{3+})		Ferrous Iron (Fe^{2+})
Trichloroethene (TCE)		cis- and trans- Dichloroethene (cis-, trans- DCE)
Vinyl Chloride (VC)		Ethene (C_2H_4), Chloride (Cl^-)
cis- and trans- Dichloroethene (cis-, trans- DCE)		VC, Chloride (Cl^-)
Sulfate (SO_4^{3-})		Sulfite (SO_3^{2-}) and Sulfide (S^{2-})
Carbon Dioxide (CO_2)		Methane (CH_4)

Figure 2-2 Terminal electron receptors and associated metabolic products in order of reaction preference.

Together these data can be used to evaluate overall reducing or oxidizing conditions within different areas of the plume. For example, nondetect nitrate, elevated dissolved manganese, elevated dissolved iron, and elevated sulfate suggests the aquifer is in iron-reducing conditions, potentially moving into sulfate-reducing conditions. The most reducing environment (methanogenesis) will have no nitrate, elevated manganese and iron, low sulfate, and elevated methane present. If nitrate is elevated and no dissolved manganese or iron is present, then the aquifer is likely in aerobic conditions.

Understanding the baseline geochemical environment is also critical for chemical remedies. In the instance of ISCO processes, background demand of oxidant is required to ensure that enough oxidant is delivered to the subsurface to overcome the background demand and still have enough oxidant concentration remaining to react with the contaminant. For some oxidants (for example, persulfate), the presence of ferrous iron can be a benefit if it is in a form and at concentrations high enough to activate persulfate without requiring the addition of another type of activator (for example, alkaline pH, hydrogen peroxide, chelated iron). If an aquifer is fairly reduced, a quantitative assessment of background demand and/or ambient activation is recommended through laboratory analysis or bench testing of the aquifer material (see Section 3.3.2), groundwater, and oxidant to ensure that the chemical amendment is properly designed to meet remedial objectives.

2.3.5.3 Secondary Water Quality Considerations

Consideration of secondary water quality impacts from amendments and subsequent reactions of in situ processes should be included during the screening step. For example, Figure 2-2 indicates that reducing conditions can liberate some metals species as a negative ORP shift can affect redox-sensitive metal speciation or produce hydrogen sulfide and metal sulfide complexes. The addition, and subsequent fermentation of a carbon substrate, will create reducing conditions in an aquifer, and if the aquifer was not already reducing, there will be a release of redox-sensitive metals (for example, manganese, iron, arsenic), color variations and an abnormal odor (surface discharge). During ISCO applications oxidation of trivalent chromium into mobile hexavalent chromium has been observed at many sites. The magnitude of concentration changes of these metals will depend on the site-specific mineralogy of the TTZ. The release of these metals is generally limited to the footprint of the TTZ, as the groundwater will restore to ambient conditions typically outside of the active reaction zone. Most of the time this is not a cause for concern, but consideration for this should be included during the evaluation, especially if a sensitive receptor is present near the TTZ (see Section 3.2.2).

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3 Amendment, Dose, and Delivery Design

The remedial design process is commonly visualized as a linear sequence (see Section 5.2) that begins with the CSM; however, in practice, the overall in situ design process is iterative and cyclical with many feedback loops at any step connecting to both earlier and later steps (see Figure 3-1). Once the CSM is developed and RDC is initiated, one or more potentially viable remedial design options are identified. This remedial design consideration is a preliminary screening of potentially viable remedial alternatives considered relative to site characteristics and treatment objectives. A design is refined and further developed once the predesign investigation is complete, and the project moves to implementation. Each of these steps is an optimization step; every step in the sequence is evaluated and the results used to improve the process for the next step or used to justify returning to an earlier step in the sequence.

3.1 The Design Wheel and Optimization Process

The design wheel involves consideration of the amendment, delivery method, and dose simultaneously throughout the in situ RDC, design, implementation, and monitoring process. Any step in the sequence can be performed again as new information becomes available. For example, during the initial evaluation of remedial design options, one or more data gaps may be identified in the CSM, and the overall process returns to improve the CSM before continuing evaluation of remedial design options. Similarly, during RDC, a site characteristic may be found to be unfavorable to the remedy under consideration, which necessitates returning to the consideration of remedial design options rather than moving forward to implementation.

Optimization Staircase

The cyclical nature defined in Figure 3-1 is extended into the implementation phase of testing and monitoring. Refinement of the design following selection of the amendment and the delivery strategy may involve various tests, all applying the dose, delivery, and amendment design feedback; results of each test feed refinements into a subsequent test. The same applies to the full-scale implementation phase, in which operational testing as well as performance testing could result in modifications to the dose, delivery, and even the amendment. For instance, during full-scale implementation the monitoring results may indicate that repetitive dosing or more frequent dosing may be required to achieve optimum performance.

Each of the steps in the stages of the optimization process (Remedial Design Characterization; Amendment, Dose, and Delivery Design; and Implementation, Monitoring, and Data Analysis; Figure 3-1) must also consider the nature of the in situ remediation amendment (e.g., liquid or solid), dose of the amendment (e.g., concentration, mass, or volume), and method of amendment delivery (e.g., liquid injection or slurry/solid injection). The nature of the amendment, delivery method, and dose are all interrelated by a cyclical process (Figure 3-1). For example, a certain amendment (e.g., an organic carbon source intended to stimulate reductive dechlorination of a chlorinated solvent) may be available in solid or liquid forms, and the liquid forms may be available in a range of concentrations. The selection of solid or liquid, and liquid concentration, in turn will affect how much of the amendment is required. The amendment may also be available in a range of viscosities or densities, which (along with the nature of the amendment as a solid or liquid, and the volume of the amendment required) may affect the method of amendment delivery. Amendment delivery options may, for example, include hydraulic or pneumatic fracturing, solid, slurry, or liquid injection via direct push methods, injection via temporary or permanent wells, etc. Thus, all three factors (amendment, dose, and delivery) are simultaneously and iteratively evaluated to develop a remedial design. Design is also implicitly considered in each stage of the remedial design sequence. For example, the data needed in the predesign investigation are determined in part by the amendment, dose, and delivery method under consideration, emphasizing the cyclical and iterative nature of the overall process. The elements of the Design Wheel (amendment, dose, and delivery) are considered further in Sections 3.4, 3.5, and 3.6.

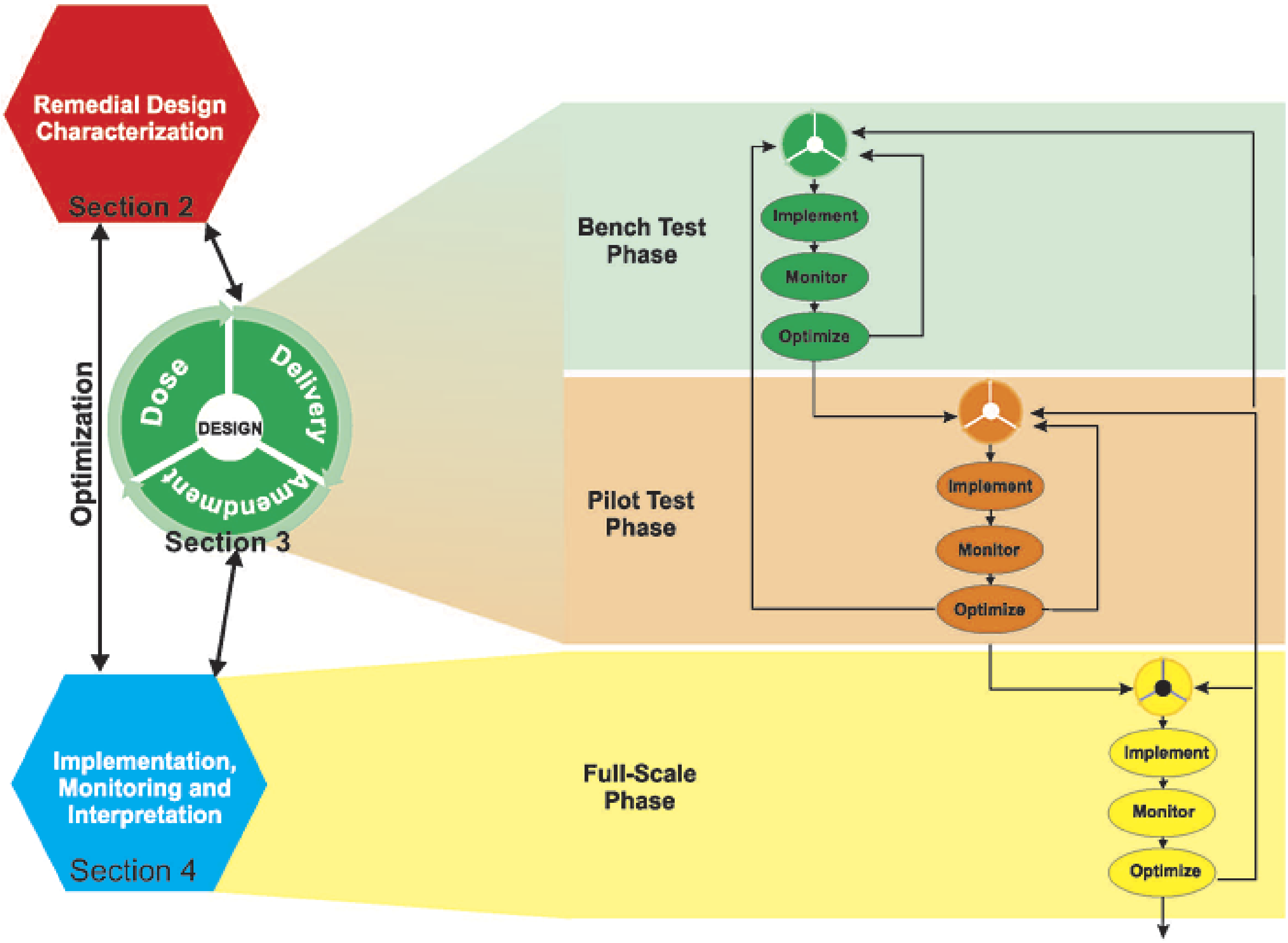

Figure 3-1. Implementation and optimization process.

3.2 Design Considerations

The following sections highlight some of the factors that need to be considered during the design process. Defining the TTZ is one of the essential first elements of remedial design. Consideration must also be given to how the selected remedy may affect subsurface conditions and the potential for secondary effects in other subsurface characteristics, in addition to the primary or desired effect. In certain situations, it may be appropriate to apply coupled in situ remediation technologies simultaneously or sequentially to effect treatment of sites (e.g., sites with contaminants in different geological units or with comingled contaminants). A final key component of the design that needs to be considered is the relationships among cost, risk, and certainty of outcome (USEPA 2016).

3.2.1 Target Treatment Zone

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The geometry and characteristics of the TTZ, including, for example, the areal extent, depth interval, geology, hydrogeology, and geochemistry, significantly influence selection of remedial amendments, amendment requirements, delivery method, and process and performance monitoring, and nearly all other characteristics of design and implementation. Like many other aspects of remedial design, definition of the TTZ is often an iterative process that considers the collateral effects, performance, cost, and other factors of a treatment approach, and is commonly revised as subsequent aspects of a design are developed.

Key considerations for defining the TTZ include:

- **Cleanup objectives**: The objective may be reduction of source area mass, protection of a particular receptor, meeting an interim remedial goal, achieving closure, or other site-specific objective. See Section 2.3.1 and (ITRC 2011c) for more details on development of cleanup objectives.
- **Spatial and temporal relationship to other remedies**: If multiple remedies are planned for a site, the TTZ for each remedy must consider how the remedies may interact with each other. For example, if ISCO is selected for a DNAPL source area and ISCR is selected for a plume area, then the TTZ for each remedy should consider downgradient transport of the ISCO amendment or its byproducts to the ISCR TTZ.
- **Uncontrolled amendment discharge**: The TTZ must consider the potential for unintended discharge of injected amendments. For example, if the potential exists for discharge of groundwater to surface water, then the TTZ should consider the potential for transport of remedial amendments to the discharge area.
- **Geologic, hydrogeologic, and geochemical characteristics**: If, for example, the remedial design is injection of a liquid amendment, and a portion of the TTZ is characterized as very low permeability clay, then the planned design may be ineffective in the low permeability clay zone. As another example, the presence of competing electron acceptors may necessitate a modification of the TTZ for a biological approach. Methods to define the TTZ can include both empirical and modeling tools. For example, typical site characterization methods (e.g., soil borings and/or wells with associated sample analytical data, or remote direct sensing methods such as the membrane interface probe (MIP) may be used to define the volume that exceeds a cleanup standard, and therefore defines the TTZ. Sample data can be augmented with data and visualization tools to quantify TTZ volumes and geometry. Many types of amendments, such as chemical oxidants and bioremediation agents, can partially or completely dissolve in groundwater and thus undergo transport with groundwater. Fate and transport can be modeled with tools such as MODFLOW in combination with MT3DMS (Zheng 2010, 1999) to estimate the potential area of influence of the amendments, and hence the resulting TTZ (which in turn can be iteratively optimized so that the TTZ reflects the area exceeding a cleanup standard). ITRC's Advanced Site Characterization (ITRC 2019). Guidance can help better define TTZs along with the associated hydrogeology and soil types.

Consideration needs to be given throughout the process to refine and optimize the TTZ so as to achieve the site goals in a desired time frame and reduce overall cost.

3.2.2 Secondary Effects

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The very nature of an in situ remedy requires some type of change to geochemical, biological, hydrogeological, and/or other characteristics of the subsurface, which results in the desired remediation. Evaluation of potential secondary effects begins with an understanding of how the selected remedy may affect subsurface conditions (see Section 2.3.5.3).

Secondary effects can also occur over a wide range of time—from transient shifts lasting hours or days to long-term changes that may last for many years. Thus, all in situ remedies should consider the potential secondary effects of the remedy design, including how to evaluate (and potentially mitigate) secondary effects, beginning with bench and field pilot tests prior to implementation of full-scale remedies (Figure 3-1).

Secondary effects to be considered during remedial design include the effects of injected amendments on groundwater chemistry.

- shifts in redox conditions and pH associated with chemical oxidants and reductants, bioremediation amendments, and other amendments, which can affect mobilization of metals, survival of microbial populations, and other characteristics
- increased concentration of amendment components in the groundwater, which can pose residual primary and/or secondary water quality issues after the target contaminant is destroyed
- partial transformation of target contaminants, potentially forming more mobile or more hazardous intermediate or final degradation products (such as accumulation of vinyl chloride (VC) from a perchloroethene (PCE) – or trichloroethylene (TCE) -contaminated site)
- discharge of injected amendments to unintended locations, such as the surface, other untargeted portions of the aquifer, or discharge to sewers, surface water bodies, and basement sumps
- Other potential secondary effects may include vapor emissions, enhanced subsurface vapor transport or indoor air volatilization, noise, site disruptions, etc.

Several common illustrations of secondary effects are associated with injection of chemical amendments. For example:

- In situ chemical oxidation with sodium persulfate may include injection of strong bases such as sodium hydroxide (for alkaline activation of the persulfate) or transition metals such as iron (for iron activation of persulfate). Collectively, these amendments are called activators and produce strong reactive species such as hydroxyl radical and sulfate radical, which can destroy a wide range of contaminants. However, large shifts in groundwater geochemical conditions such as oxidation-reduction potential, pH, and sulfate concentration can result in significant secondary effects, such as effectiveness of treatment, precipitation of inorganics (e.g., metals), and adverse effects to sensitive receptors.
- The addition of sodium persulfate can affect the natural or anthropogenic chromium present in the soil or aquifer matrix, which may be oxidized to hexavalent chromium, a carcinogen that is soluble and mobile under the oxidizing geochemical conditions. This condition could expand downgradient due to advection of the impacted groundwater. The byproduct of chemical reduction or oxidation is not necessarily the cause of secondary water quality impacts, but the addition of the reagent itself can be. For example, sulfate has a secondary drinking water standard of 250 mg/L (USEPA Drinking Water Standards) The addition of persulfate or magnesium sulfate (Epsom salt), for example, will increase the sulfate load to an aquifer, potentially leading to an exceedance of this standard. Similarly, manganese has a much lower secondary water quality criterion of 0.05 mg (USEPA Drinking Water Standards); therefore this may be a design consideration for permanganate addition near sensitive receptors.
- The addition of a carbon substrate often will result in methane production when all available electron acceptors have been depleted and excess labile carbon remains (see Section 3.5.2 Fermentation of organic carbon will produce compounds such as acetate and hydrogen, which methanogenic bacteria (e.g., archaea) can directly be used to produce methane under anaerobic conditions (Schink 1997). This can be a concern if carbon substrate amendment is being deployed near buildings because methane is explosive when present as 5% v/v of the surrounding atmosphere (NIOSH 2006). Using an average Henry's law constant for methane (Sander 1999), the equivalent dissolved gaseous concentration associated with 5% atmospheric concentration is less than 2 milligrams per liter (mg/L). In many cases this may not be an issue, for example, if there are no structures nearby, or if enough vadose zone is present to allow the dilution and degradation of methane by aerobic organisms (methanotrophs) to occur prior to reaching the land surface (ITRC 2011a). Steps should be taken to evaluate the potential for explosion risk in other environments where dilution and degradation cannot occur (e.g., shallow depth to groundwater) or where structures are present that would allow for gas accumulation during carbon substrate amendment applications.

The modeling tools for remedy design summarized in Section 3.3.1 can also be applied to evaluate these secondary effects. For example, PHREEQC, from the U.S. Geological Survey, can be used to assess the potential oxidation and downgradient transport of hexavalent chromium associated with an in situ chemical oxidation treatment.

3.2.3 Coupled Technologies

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In situ remediation technologies can be applied simultaneously or sequentially to affect treatment of comingled contaminants; however, the longevity and nature of any lingering conditions that may adversely affect the second technology must be understood prior to full-scale implementation. An example of this is when TCE is chemically oxidized followed by monitored natural attenuation. Chemical oxidation will significantly decrease indigenous microbial populations and recovery of the degrader microorganisms will take time before they can contribute to natural attenuation. The recovery period should be factored into the assessment of whether this combination will meet site cleanup objectives within the necessary time frame. The recovery period may be shortened by addition of amendments and bioaugmentation; however, this would become enhanced in situ bioremediation instead of monitored natural attenuation (Appendix E.14, Naval Submarine Base Kings Bay Case Study). [Please see (ITRC 2011c) section 4.2 for additional information on this topic.] It should be noted that some reagents have an initial remediation process followed by a different process.

3.3 Design Support Elements

This section describes the design elements that are used to support in situ remediation design. These elements are an extension of the CSM and RDC data (see Section 2). The number one source of failure for amendment injection to meet remedial treatment objectives is the lack of an adequately detailed lithologic characterization of the TTZ. A remedial design that minimizes uncertainty often includes a bench study to identify the proper amendment and dosing requirements. This is followed by a pilot study to understand injection rates, distribution pattern around injection points (ROI); (see Section 3.7.1 for a discussion of distribution vs. ROI), and any site-specific conditions adverse to amendment placement (i.e., tendency for amendment to daylight at the injection site or nearby locations) (ITRC 2017a). With these parameters properly understood, the greatest source of uncertainty and failure is the reliance on overly simplified subsurface conceptual models. Design elements used to support in situ remediation design include modeling/analytical tools, laboratory bench testing, and field pilot testing. Each is discussed in the follow subsections.

3.3.1 Modeling and Analytical Tools

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Analytical and numerical models for parameter estimation, groundwater flow and transport, and/or geochemical reactions can be used to assist with the design and optimization of in situ remediation. The application of models can range from simple spreadsheet calculations to complex three-dimensional models, depending on the scale and complexity of the remediation project. The selection of a model depends on the question(s) that needs to be answered and the data available to support the modeling effort. Models are one of many tools that can be used at any phase of an in situ remediation project, including development of the CSM, feasibility study, design, implementation, and review of the results. However, not all projects will need to use a model, and the complexity of the model does not necessarily improve the output or accuracy of the model due to the inherent uncertainty when working in heterogeneous geologic systems.

Table 3-1 outlines some of the models that can be used to support in situ remediation projects, provides a brief description of the model, and a source for additional information. Some of the software is public domain and other models are commercially available and require a license. Spreadsheet tools have been developed by many practitioners to support remediation projects. Spreadsheets allow rapid iteration on the design of an in situ remediation program, e.g., assessment of injection duration over a range of flow rates, or calculation of possible lateral transport assuming cylindrical distribution as a function of volume injected and effective porosity. This list is not an endorsement for any of the models, and other models may be available beyond those that are listed here (ITRC 2011c).

Table 3-1 Models that can be used to support remedial design ▼*Read more*

Model	Type of Solution	Application	Availability
BioPIC	Macro-based spreadsheet decision tool	Used to evaluate remedial pathways for remediation of chlorinated ethenes.	(Lebron 2011)
BIOSCREEN	Spreadsheet-based screening model	Simulates remediation through natural attenuation of dissolved hydrocarbons at petroleum fuel release sites. The model generates biological attenuation rates under current conditions based on known concentration versus time/location.	(USEPA 1997)

Model	Type of Solution	Application	Availability
CORT3D	Finite difference, 3-D reactive transport model based on modified versions of RT3D and MODFLOW	Can be used to perform detailed simulations of ISCO treatment. Incorporates DNAPL dissolution, sorption, oxidant-contaminant reactions using second-order kinetics, kinetic natural oxidant demand, and diffusion of oxidant and contaminant.	Download Technology Practice Manual. Model is contained in zip file under ISCO Supplemental Info & Tools. (SERDP 2006a)
Conceptual Design for ISCO (CDISCO)	Spreadsheet-based tool that models radial oxidant transport and persistence	Can be used to assess the lateral distribution of oxidant from an injection point. This tool was developed for permanganate but could be applied to other oxidants or potentially to amendments other than oxidants.	Download Technology Practice Manual. Model is contained in zip file under ISCO E-Protocol for Site Specific Eng & App. (SERDP 2006b)
Emulsion Design Tool Kit	Spreadsheet-based tool	For design of distribution of emulsified oil or substrate to promote bioremediation.	SERDP n.d.
MODFLOW Family of Codes	3-D finite difference code for modeling groundwater flow and transport	Can be used to model groundwater flow and transport, amendment flow, geochemical conditions, variable density flow.	MODFLOW and related programs
Natural Attenuation Software (NAS)	Software package that provides a decision-making framework for determining the time needed to clean up groundwater contamination sites.	• Compares times of cleanup associated with monitored natural attenuation to pump-and-treat remediation • Expands the kinds and numbers of contaminants considered • Allows for concurrent consideration of solvents (chlorinated ethenes) and petroleum hydrocarbons	NAS was developed by the U.S. Geological Survey (USGS).
PHREEQC V-3	Graphical user interface for geochemical computer program (PC only)	A computer program for speciation, reaction path, advective transport, and inverse geochemical calculations.	USGS – PHREEQC version 3
REMChlor	Analytical solution	Remediation of either the source zone and/or plume area can be evaluated. Model includes unique degradation rates for parent compounds (e.g., PCE, TCE) and byproducts (e.g., cis-DCE and vinyl chloride). At sites with sufficient data, the model can be calibrated to determine site-specific flow and decay parameters and used to estimate future concentrations with and without remediation.	(USEPA 2007)
SEAM3D	3D finite difference	Simulation of complex biodegradation problems, including code that can simulate biodegradation, NAPL dissolution, co-metabolic biodegradation, and reductive dechlorination.	Report document and code available: (USACE 2000)

Model	Type of Solution	Application	Availability
Substrate Design Tool	Spreadsheet-based model	Can be used to estimate amendment mass requirements for anaerobic bioremediation projects. Model incorporates consumption of competing terminal electron acceptors (dissolved oxygen, nitrate, sulfate, etc.) as well as target compounds. The flux into the treatment zone over the design life of the system can be included.	(SERDP 2006c)

3.3.2 Laboratory Treatability Bench-Scale Testing

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This section focuses on key considerations of how treatability (bench) test results can be incorporated into the design and optimization process. Laboratory bench testing (e.g., bottle/jar test, batch test, column study, microcosms, reactors) has been used to provide proof of concept for the use of in situ treatments since the 1980s. It remains an important tool that can be used to help determine the type and dosing of amendments in situations where the chemistry is complex and/or multiple treatment steps may be necessary. Bench-scale testing is one of many tools that can be used and may not provide added value for all sites. The decision to use bench-scale testing should be evaluated based on site-specific requirements, which could include the scale of the site, project timeline, level of understanding of the contaminants and potential reactions, site chemistry, and/or the need to evaluate alternate treatment options.

Bench-scale testing typically refers to tests that are conducted in batches (e.g., bottles) or to dynamic tests (e.g., column studies). Batch testing typically involves mixing soil with a water-based solution (e.g., groundwater with amendment) and mixing (e.g. agitation, tumbling, continuous stirring) or allowing to sit without mixing. These tests are generally cheaper and of short duration (days to weeks; rarely more than 6 months). Column studies periodically or continuously exchange the water-based solutions and can pulse an amendment followed by an unamended solution or continuously pulse a solution impacted with COCs to look at depletion of an amendment. More detailed experiments are generally conducted over the period of months to evaluate longer term behaviors of a system. Over the full range of bench test level of effort, variables in addition to general configuration and duration can include:

- solid material (e.g., site soil) that can be used in various methods
- mixing and homogenization
- repacked column
- undisturbed continuous core sample
- treatment of solids
- sterilization
- inoculated with bacteria
- nonsterilized and noninoculated impacted solids
- controlled dosing of contaminants onto background solids
- liquid solution
- site groundwater
- water that will be used to mix amendment
- amendments: Can refer to chemical compounds, natural or synthetic chemical additives, and/or commercially branded remediation products used to achieve desirable physical and biogeochemical conditions within the test environment.
- buffers
- biological (e.g., bacteria)
- activators
- other constituents
- pH
- moisture content
- soil density
- aerobic/anaerobic conditions

- temperature
- redox conditions

Many decisions go into designing a bench-scale test, such as the number of replicates, how to establish control samples, the test duration, analytical sampling strategy, and how to manage volatilization and/or sorption.

Bench tests generally do not represent field conditions due to issues of scale, field heterogeneity, amendment transport in the subsurface, reaction kinetics, and other physical or chemical characteristics that cannot be captured in the laboratory within project constraints. Despite these limitations, bench test results can provide an initial, screening-level evaluation of potential outcomes, suitability of an amendment for a site, and potential effects of treatment. This information can then be used to inform and optimize the implementation of a field pilot test or field remedial design, and/or provide insight into how to establish a monitoring program for field implementation.

Bench-scale tests should be designed to answer predetermined objectives that are specifically defined by field design unknowns and should support pilot- and full-scale remediation planning. General project objectives that might be effectively addressed through bench testing include:

- general efficacy of a treatment technology
- contaminant destruction removal efficiency (DRE)
- reagents/amendments and associated dosage levels
- sequential testing of different amendments
- assessment of a new or alternative process
- the effectiveness of different activators
- performance assessment monitoring techniques
- quantification of potential secondary effects

In designing the bench-scale study, the question, “How will this information improve application in the field?” should be asked to help optimize the tests.

3.3.3 Field Pilot Tests

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Pilot tests are small-scale, preliminary field events conducted to evaluate feasibility, time, cost, adverse events, design assumptions, and unexpected responses to generally improve upon the remedial design prior to implementation of a full-scale remediation project.

The complexity and scale of pilot tests can vary depending upon the objectives and requirements. In general, a pilot study plan can be used to guide the pilot test, identify the objectives of the pilot test, and identify the anticipated outcome of the test. The plan can include details on the method for amendment injection, parameters to be monitored during the pilot test, the duration of the pilot test monitoring, and the anticipated results. Developing a plan will help facilitate the evaluation of internal (e.g., injection method) and external (e.g., heterogeneity) factors that affect the test results, and help identify problems with performance.

Pilot tests are generally more representative than bench tests of what can be expected during the full-scale application of a remediation effort because they are performed at the site under site-specific in situ conditions. The primary benefit of a pilot test is to reduce the uncertainty associated with the in situ injection, but it also has the potential to provide cost savings at larger or complex sites. Pilot tests cost more and require more time to implement than bench-scale testing. So the benefits of additional information to reduce uncertainty versus implementing a conservative design will need to be evaluated. Pilot tests are not required for every site. For example, at a relatively small site, the benefit of a pilot test to improve and optimize an injection design is outweighed by the cost of additional mobilizations, sampling, laboratory costs, documentation, and time required to implement, evaluate, and incorporate the results of the pilot into a full-scale design. In these cases, if the CSM and the behavior of the selected amendment are both well understood, it may be more cost-effective to implement a more conservative full-scale design.

The data and information derived from a pilot test should be used to reduce uncertainty and optimize the full-scale injection. For example, the ability to observe the results of the pilot test in a downgradient well could mean that the injection spacing could be farther apart. Therefore, before conducting a pilot study, it can be beneficial to review the type of data that can be monitored and the design parameters that can be specified in the design specifications. Then based on the anticipated site-specific challenges, the pilot plan can include the necessary parameters to be tested, and locations for data collection, to address the design specifications. These can include:

- injection flow rates versus pressures limitations necessary to avoid surfacing, fracturing, or groundwater mounding
- demonstration of feasible drilling methods
- distribution and/or ROI to optimize injection locations to potentially lower drilling costs
- the ability and time to achieve target depths with proposed drilling technology
- refusal conditions and how to overcome them, or how to incorporate top of bedrock data into the CSM
- assessing whether boreholes for packer injection or emplacement can stay open or need to be cased
- adverse impacts on injection tooling due to difficult drilling conditions
- the ability of mixing and pumping equipment to effectively mix and inject amendments
- the ability of the target formation to accept the design injection volume without excess mounding or surfacing
- a better understanding of seepage velocity versus assumed or measured values
- residence time of the amendments within the ROI, which is impacted by the groundwater flow rate and biodegradation kinetics
- evaluation of survivability of bioaugmentation cultures in situations where conditions may be detrimental to survival
- any unexpected safety considerations

In addition to the parameters that will ultimately be defined as part of the design specifications, a pilot test can also address other concerns that can influence the effectiveness of the treatment rather than just the mechanisms of injecting the amendment. So developing the specific range of objectives for the pilot test will help define the type of information that needs to be collected. For example, depending on the site, it may be beneficial to collect information that allows for evaluation of the:

- applicability and performance of the remedy in heterogeneous site conditions (Appendix E.9 In Situ Bioremediation and Soil Vapor Extraction at the Former Beaches Laundry & Cleaners Case Study)
- remedy time frame under real world conditions, reflecting the combined effects of dilution, advective flow, diffusion, adverse chemical interactions, etc.
- parameters that will be required for the full-scale design
- dose (i.e., concentration, mass, or volume), frequency, and timing
- potential geochemical impacts or other secondary effects to the aquifer, such as mobilization of metals or acid production
- locations and distance from injection points both horizontally and vertically for sampling and performance monitoring
- amendment distribution vertically within the injection zone and laterally
- treatment ROI (see Section 3.7.1 for a discussion of distribution vs. ROI)
- contaminant treatment efficacy and byproduct formation

After injection and during the monitoring period for the pilot test, the data should be evaluated to look for anomalies. For example, if the reaction was expected to release iron, but no iron is detected, what does that mean about the reactions and processes occurring on site? Is the issue related to the time required for the reaction? Does it have any implications for the dose of amendment added? Does something need to be analyzed during the pilot test to help answer these questions? How would the variation from the anticipated results affect the end result?

As the results are scaled up, the data must be carefully evaluated to ensure that extrapolating from a pilot study to full-scale environmental remedy accounts for the inherent variability of the site and other uncertainties. Considerations to evaluate from the pilot test include:

- optimization of flow rates versus pressures
- verified distribution and/or ROI (to either increase or decrease planned injection location spacing). If flow rates are lower than expected this can be overcome with manifolding to install additional injection locations simultaneously.
- logistics associated with larger effort, e.g., water management, amendment delivery and storage
- pre- and postinjection sampling temporal requirements

- heterogeneities
- additional resources
- time frames
- equipment (e.g., rental or purchase)

The pilot test results should be used to verify the design elements, process monitoring, and implementation because the pilot test is a field-scale application of the remedy. Some aspects of the design may be specific to the pilot scale (e.g., significantly denser monitoring network and more frequent monitoring); however, in general the information in Section 4.4 applies to both the pilot- and full-scale applications.

3.4 Amendment Selection Considerations

This section offers descriptions of the main amendment types, target contaminants, typical delivery methods, and links to fact sheets from the Treatment Type column in Table 3-2. The fact sheets describe limitations of each amendment, the elements to consider that are design-specific, health and safety issues, references, and some case studies.

The selection of amendment(s) and injection technologies may affect each other and should be considered in an iterative process taking into account site-specific factors such as infrastructure and physical limitations, geology/hydrogeology, and client preferences or regulatory requirements as identified in the CSM. In addition, location of the TTZ (within the source area or the downgradient plume) should also factor into the amendment selection and dosing. The amendment selection information in this section is presented independent of delivery methods. In Section 3.8 (Delivery Strategies), delivery technologies are described and a matrix assists in the consideration of applicable delivery technologies based on site-specific conditions (see Section 3.8).

Differences in treating the source versus treating the plume are critical when selecting amendments. For example, in a source zone, for some amendments, you might consider injecting the *amendment* at a much higher concentration to deliver more of the *reagent* in a smaller volume and have a more aggressive treatment. By contrast, in a plume area, you might consider injecting the same amendment at a lower concentration but in a greater relative volume because distribution over a wider area is more important than delivery of a large dose to a small area.

Table 3-2 provides information about amendment types and is organized primarily by treatment processes and treatable contaminants. This allows a user, with a known list of target COCs, to access a suite of applicable amendments and screen out options that would not be appropriate for remediation of the COCs. For instance, a project designer who is looking to use in situ injection technologies to remediate dissolved-phase concentrations of benzene, toluene, ethylbenzene and xylene (BTEX) in groundwater can consult the matrix in Table 3-2 and immediately identify amendments, such as a peroxide compound or other oxygen delivery method, as being more effective than a vegetable oil-based product. The table also describes the function of each amendment (e.g., oxidation, aerobic degradation enhancement compounds, anaerobic degradation enhancement compounds, surfactants, etc.) so that the user can further evaluate the potentially applicable amendments and limit the options to those that provide an appropriate function. The table links to additional information (fact sheets) on suitability for remediating contamination in various media, suitability for treatment of various soil types, cost, expected active lifespan for the amendment, suitability with delivery technologies, advantages over other amendment types, and potential limitations of the amendment.

In many instances the use of a laboratory batch or column test should be considered during the amendment selection process, not only to inform the efficacy of the amendment for a particular project, but also to estimate potential remedial design parameters that will be further refined (e.g., pilot testing). Many amendments blur the lines between biotic and abiotic applications. The amendments are grouped under biotic, abiotic and other additives (Appendix A1 Biotic Amendment Fact Sheets, Appendix A2 Abiotic Amendment Fact Sheets, and Appendix A3 Other additives Fact Sheets), in what we believe are the primary applications, but recognize that any amendment may be considered in multiple sections.

Table 3-2. Amendment types and typical injection/emplacement technologies ▼*Read more*

Treatment Type	**Description/Summary**	**Target COCs**	**Typical Injection/Emplacement Technologies Methods**

Treatment Type	**Description/Summary**	**Target COCs**	**Typical Injection/Emplacement Technologies Methods**
Common Biotic Amendments (A.1)			
Aerobic bioremediation (A1.1)/ biological oxidation	Aerobic degradation occurs predominantly in near-surface saturated and vadose zone environments. (Only for sparging. Calcium peroxide does not work in vadose zone). Naturally occurring aerobic microorganisms are widely dispersed, and usually react efficiently with supplemental oxygen provided via bioventing, air sparging, or if necessary, amendments that release oxygen; low to moderate doses of hydrogen peroxide, calcium peroxide, or magnesium peroxide.	• Petroleum hydrocarbons and some fuel oxygenates (e.g., methyl tertiary-butyl ether [MTBE]).	• Air/ozone direct injection • Air sparging/biosparging • Introduction of oxygen via diffused emission • Direct vapor phase injection
Cometabolic aerobic & anaerobic bioremediation (A1.2)	Co-metabolism involves degradation of contaminants using enzymes produced by microorganisms as a result of consumption of a primary substrate such as methane, propane, ethane, etc. that may be injected into the subsurface. The microorganisms do not benefit from the degradation process and can thrive in the absence of the contaminants. Most co-metabolic processes occur under aerobic conditions and may require oxygen additions to stimulate/support degradation.	• Chlorinated solvents (TCE, DCE, VC, DCA) • Chloroform • MTBE • 1,4-dioxane • THF • Explosives • Atrazine • PAHs • Some pesticides	• Trenching/soil mixing • Direct push injection • Permanent injection wells • Biosparge wells for gases
Anaerobic (A1.3) biological reduction	Contaminants are degraded via a reductive process by certain types of microbes under anaerobic conditions. Fermentable organic substrates are injected or placed into the subsurface to enhance the production of hydrogen, which is in turn used by the microbes in the reductive reactions.	• Chlorinated solvents • Many pesticides and munitions • Certain inorganic compounds • Petroleum hydrocarbons (typically by introduction of electron acceptors such as nitrate and/or sulfate)	• Direct push injection • Permanent injection wells • PRBs

Treatment Type	**Description/Summary**	**Target COCs**	**Typical Injection/Emplacement Technologies Methods**
Bioaugmentation (A1.4)	Bioaugmentation consists of adding microorganisms to the subsurface to enhance and further promote the biodegradation of contaminants under either aerobic or anaerobic conditions. Microorganisms may be cultivated using indigenous populations at the site or using special strains that target specific contaminants. Note that bioaugmentation may involve aerobic or anaerobic bacteria, and that one or more of the biostimulation methods (e.g., addition of electron donors or acceptors), described above in the bioremediation rows, is typically required for bioaugmentation cultures to be prominent in the subsurface.	• BTEX • Jet fuels • Kerosene • Chlorinated solvents • Certain explosives and pesticides • 1,4-dioxane	• Direct push injection • Permanent injection wells • Injection wells particularly for PRBs
Abiotic Amendments (A2)			
Chemical oxidants (A2.1)	Oxidants delivered to the subsurface degrade or transform contaminants via oxidation and reduction reactions in the vadose and saturated zones. Oxidants can be used for source area remediation in conjunction with other compatible remedial alternatives to address downgradient areas with dissolved-phase or lower concentrations. Reaction rates depend on temperature, pH, reactant concentrations, activators or stabilizers, reaction byproducts, natural organic materials, and oxidant scavengers. Activators, stabilizers, and chelating agents may be used to enhance the subsurface oxidation reactions.	• BTEX • MTBE • TPH • Chlorinated solvents • SVOCS • Energetics • 1,4-dioxane	• Trenching/soil mixing • Direct push injection • Permanent injection wells • Soil mixing • Permeability enhancement (i.e., environmental fracturing) • Recirculation • Slow-release oxidant cylinder (Evans 2018) • Ozone sparging
Chemical reducing compounds for degradation enhancement (A2.2)	In general, reducing agents degrade or chemically transform contaminants into potentially less toxic and less mobile forms. The reductive processes depend on the contaminant, the type of reduction, and natural processes in the subsurface.	• Metals and metalloids • Chlorinated solvents • Energetics	• Trenching/soil mixing • Direct push injection • Permanent injection wells for very fine zero-valent iron (ZVI) products and calcium polysulfide • Hydraulic and pneumatic emplacement

Treatment Type	**Description/Summary**	**Target COCs**	**Typical Injection/Emplacement Technologies Methods**
Biogeochemical transformation (A2.3)	Biogeochemical transformation collectively describes the physical, chemical, and biological processes induced by reduced iron and sulfur minerals, transforming contaminants into nontoxic end products. Multiple transformation pathways often result in full mineralization. Reduced iron is obtained from naturally occurring geological formations, introduced reduced minerals, or microbial activity under anaerobic conditions. Reduced sulfur is obtained from sulfate, is naturally present, or is added with the carbon-based electron donor. It can also be used as a component of MNA under favorable subsurface conditions.	• Chlorinated solvents • Pesticides • Explosives • Heavy metals	• Direct push injection • Permanent injection wells • Trench-based permeable reactor
Activated carbon–based injectates (A2.4)	The primary mechanism for contaminant reduction using absorptive media (activated carbon) is via adsorption, which may be followed by degradation of the compounds by a secondary process such as reaction with ZVI, ferrous sulfide, persulfate, or biological reactions facilitated by electron acceptors such as oxygen, nitrate, and/or sulfate.	• Petroleum hydrocarbons • Chlorinated solvents	• Trenching/soil mixing • Direct push injection for slurry or colloidal forms • Injection wells for fine colloidal forms • Hydraulic and pneumatic emplacement • Emplacement (soil mixing or trenching) for solid or slurry forms
Surfactants & co-solvents via solvent flushing (A2.5)	Surfactant formulations are used to recover free-phase NAPLs via mobilization by reduction of the NAPL/water interfacial tension (surfactant flooding) or via solubilization by formation of micelles that contain droplets of the NAPL or simply by monomer detachment of a contaminant molecule from the NAPL or adsorbed phase. Surfactant formulations include aqueous solutions containing a surfactant and electrolyte, and sometimes a cosurfactant. Often a shear thinning polymer fluid is necessary to achieve high-level mobilization performance. Solvent flushing involves using low molecular weight alcohols to solubilize and/or mobilize free-phase NAPL.	• Free-phase NAPLs, including:Petroleum hydrocarbons • Chlorinated solvents • Coal tar • Polychlorinated biphenyls • Creosote	• Permanent injection wells
Other Additives (A.3)			
pH Buffers (A3.1)	Processes that inhibit pH changes in an aquifer are called pH buffering processes. These processes are important because pH is often a key control on the chemical and microbiological processes responsible for contaminant remediation.	• Contaminants subject to bioremediation	• Direct push injection • Permanent injection wells • Mixing with select amendment

Treatment Type	**Description/Summary**	**Target COCs**	**Typical Injection/Emplacement Technologies Methods**
Nutrients (A3.2)	In addition to a readily degradable carbon source, microorganisms also require nutrients such as nitrogen, phosphorus, and potassium (N, P, and K) for cellular metabolism and therefore successful growth. Vitamin B_{12} may stimulate ERD of chlorinated solvents.	• Contaminants subject to bioremediation	• Trenching/soil mixing • Direct push injection • Permanent injection wells
Methane inhibitors (A3.3)	In environmental remediation applications, methane inhibitors can be used as a supplement to EISB and ISCR amendments, rendering them safer and more effective.	• Contaminants subject to bioremediation and in situ chemical reduction	• Supplied as a water-soluble powder that can be mixed on site and added in conjunction with the electron donor (or as a component of some electron donor formulations) before injection through permanent injection wells or temporary push points.

3.4.1 Combined Remedies—Spatial and Sequential Remedies and Mixed Contaminant Options

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Some plumes have a mix of contaminants, some of which are susceptible to oxidation and/or aerobic bioremediation and others of which are susceptible only to reduction and/or anaerobic bioremediation. There are several options for treatment of these plumes, including combining remedies either spatially, where the sources or plumes may not overlap, or where one is treated in one area and the other downgradient; or sequentially, where one is treated followed in time by treatment of the other contaminant type. Secondary effects of remediation amendments (see Section 3.2.2) are key considerations when treating mixed contaminants since the effects need to be taken into consideration for multiple remediation approaches. Examples of this combined remedy approach include:

- reductive treatment with electron donors to reduce chlorinated solvents followed by aerobic polishing of the petroleum hydrocarbon (either in the same treatment zone or downgradient)
- aerobic biodegradation or in situ chemical oxidation treatment of the petroleum followed by substrate and bioaugmentation culture injections and pH adjustments to promote anaerobic bioremediation
- activated carbon–based injectates inoculated with microbes and/or nutrients to enhance the colonization of the activated carbon with microbes

3.5 Amendment Dose Requirements

Several sequential steps are typically required to estimate the amount of amendment that must be injected for any remedial design. Amendment dose here is used broadly to be applicable to volume, concentration, addition rates, and mass. Another consideration is the persistence of the amendment (e.g., electron donors such as lactate that are completely miscible with groundwater versus donors such as emulsified vegetable oil that stick to the geologic media and are dissolved/released slowly over time). The first step is to define the size (e.g., volume and contaminant mass) of the TTZ (see Section 3.2.1). The second step is to evaluate the *background demand* for the amendment, which reflects the amount of amendment required to establish and maintain the appropriate conditions for optimal remedy performance. The third step is to evaluate the *target demand* for the amendment, which reflects the amount of amendment required to destroy the target contaminant. An approach is outlined in this section to estimate the total amendment requirement for the TTZ. The amount of amendment required per injection point, or other distribution mechanism, is a factor of the delivery method, which is addressed in

Section 3.5.3, and degradation kinetics for the amendment.

3.5.1 Background Demand

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Amendments injected into the subsurface are generally intended to alter the ambient conditions in the treatment area to achieve the desired reactions with the contaminants. The amendments therefore react in some way with the soil and groundwater constituents (in addition to the target contaminants) to establish and maintain the desired condition. The amount of amendment required to address this demand is referred to as the background demand. The reactions associated with the background demand do not necessarily prevent the desired reactions between amendments and target compounds from occurring, but rather represent an amendment requirement that is in addition to the amount specifically required for reactions that transform the target contaminants. The background demand is often much higher than the target contaminant demand; in some cases, the background demand (particularly for oxidants) can be so high that a remedy becomes impractical due to technical or cost constraints. Thus, it is important to assess the background demand and incorporate it into the remedial design. Bench tests are commonly used to evaluate the background demand (see Section 3.3.2).

Background demand encompasses several types of processes depending upon the type and form of the amendment. A liquid or gaseous amendment will permeate through a soil matrix and interact with the surfaces of the soil particles. If the amendment is delivered to the saturated zone, it may also interact with constituents dissolved in groundwater. With liquid or gaseous amendments, it is therefore important to consider reactions with both soil solids and with groundwater, although in practice the soil often exerts a much larger background demand than the groundwater. An example of this type of background demand is natural oxidant demand. In other cases, if the amendment is delivered in a solid form such that migrating groundwater reacts with the surface of the solid amendment particles (for example, with ZVI), the background demand from reaction with the groundwater is generally more significant than from reaction with soil. An additional factor to consider for longer term processes is the potential for ambient groundwater flow to transport additional reactive constituents into the treatment zone.

Special consideration must be given to background demand for amendments that rely upon catalytic reactions, or for which other amendments are used as stabilizers or conditioners. An example of this type of system is catalyzed hydrogen peroxide for ISCO. Hydrogen peroxide will readily form surface complexes and react with transition metals such as iron on mineral surfaces. Therefore, practitioners often inject other amendments with the hydrogen peroxide to achieve a desired pH range or to stabilize the hydrogen peroxide reactions, which may change the background demand. Care must be taken to account for reaction conditions in the case of complex amendment mixtures.

Bioremediation amendments also have special considerations for background demand assessment. Background demand for bioremediation amendments reflects the availability of the amendment for biological metabolic reactions, the presence of appropriate microbes to metabolize the amendment, and biological reactions with competing electron acceptors (for anaerobic systems) or donors (for aerobic systems). Competing electron acceptors for anaerobic bioremediation amendments provide an example. Competing electron acceptors present in groundwater are typically consumed (microbially reduced) in a very predictable order: first dissolved oxygen, then nitrate, manganese, iron, sulfate, and carbon dioxide (see Section 2.3.5.2). Iron and manganese may be present as solid-phase minerals in the aqueous phase and can be available as electron acceptors. When designing anaerobic bioremediation injections, the design should consider both the electron acceptors that are initially present in the treatment zone and those that will flow into the treatment zone with ambient groundwater flow. Several software tools are available to help with estimation of background demand, particularly for bioremediation applications (see Section 3.3.1).

3.5.2 Target Demand

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The contaminant mass and distribution can exert a significant amendment demand or a negligible demand (relative to the background demand) depending upon the remedy and site characteristics. With bioremediation remedies, once the initial background demand is met, any additional amendment demand predominantly reflects the demand to maintain those conditions throughout the treatment period—for example, additional electron acceptors or donors that migrate into the treatment area with groundwater flow or consumption by microbial population. In this case, there is no direct reaction between the amendment and the contaminant, and the contaminant mass primarily affects how long the bioremediation conditions must be maintained (i.e., how long must the background demand continue to be met) for the microbial activity to destroy the contaminants.

With chemical oxidation and reduction remedies, the amendments typically react directly with the contaminants, and thus the contaminant mass or concentration must be considered. In the case of chemical oxidation, the total amendment demand is often arrived at by estimating the background demand as outlined in Section 3.5.1, and then estimating an additional demand based upon the amount of oxidant required to destroy the target contaminant mass. With some remedies the reactions involved are not instantaneous, and thus the contaminant concentration and a residence time in the treatment zone are factors to consider for amendment demand. An example of this is ZVI chemical reduction in a permeable reactive treatment zone (PRTZ) remedy. Reaction rates for many contaminants with ZVI are sufficiently slow that half-lives may be measured in minutes or hours. The number of half-lives (and therefore the residence time, and the corresponding amount of amendment required) is a function of the concentration of the contaminant flowing into the treatment zone and the desired concentration flowing out of the treatment zone.

The distribution of the contaminant between groundwater and soil, and between high and low permeability zones, must also be considered in the amendment requirement. For example, even if soil contaminant concentrations meet the treatment objectives but groundwater concentrations do not, then the amendment requirement must continue to reflect both the groundwater and soil mass because the contaminant desorption from the soil may continue to impact groundwater.

Injected liquid amendments will preferentially flow through relatively transmissive zones within a formation. In late-stage plumes, much of the contaminant mass may be present in less transmissive zones and the remedy must account for long-term desorption (back-diffusion) from the less transmissive zones, resulting in longer periods of treatment, which translates to a larger background demand.

3.5.2.1 Examples of Amendment Requirement Estimation Methods

Several different methods can be used to estimate amendment requirements. The overall framework is to estimate the amendment requirement based upon the volume and characteristics of the TTZ coupled with the demand from both background and contaminants within that TTZ. A quantitative approach is commonly a more effective basis for an initial estimate, which can then be refined and optimized based upon experience and/or pilot test results. Software modeling and amendment estimation tools are also available (see Section 3.3.1). Three methods can be used individually or in sequence:

- **Method 1**: Stoichiometric plus background calculation. The total amendment requirement is the sum of the demand from reaction with the estimated contaminant mass (e.g., from a stoichiometric degradation reaction) plus the demand from competing side reactions, such as with transition metals and/or natural organic carbon in the subsurface. This method is limited by the accuracy of contaminant mass estimates and the reactivity of the compounds that account for the competing side reactions.
- **Method 2**: Experienced based. Apply amendment loading rates that have been successful at other sites with similar geology, geochemistry, and plume characteristics. Although not as quantitatively supportable as Method 1, practitioner experience should not be discounted as an effective method to evaluate amendment requirements. However, all in situ remediation designs should be site-specific. Additionally, because many historical in situ remediation designs have not led to attainment of target end points, extreme care should be taken that practitioner experience that led to past failed application should not be the basis for future design.
- **Method 3**: Pilot test results. Perform a pilot test with an amendment dosing based on one of the above methods and use the resulting process and performance data to evaluate amendment requirements for future injections or a full-scale remedy.

Each of the methods outlined above is subject to significant uncertainty, thus incorporating a safety component is often prudent with amendment requirement estimates. After arriving at a conceptual design with one or more of the methods outlined above, evaluate the need for an additional safety factor to account for uncertainties such as degree of heterogeneity, accuracy of bench- and pilot-scale testing to full-scale site conditions, etc. (see Section 3.3.3). Amendments are the component of the remedy that ultimately result in subsurface treatment; however, amendments are often a relatively small component of overall project cost relative to other project management, labor, mobilization, equipment, and other costs. Read less

3.5.3 Volume Considerations

This section describes how to determine the overall volume of amendments, usually diluted in water that should be delivered. The considerations are fundamentally different depending on if the remediation program is designed to deliver a soluble amendment through pore space (*injection of liquid*) or to modify the subsurface permeability by pressurized application of a slurry (*injection of a solid*). Given these differences, discussion of volume delivered is subdivided below for injection of liquid versus injection of solids.

3.5.3.1 Volume for Liquid Injection

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The volume of a liquid amendment injected is perhaps the most important design parameter because the volume injected is closely related to the degree of contact between the amendment and contaminants that occurs in the subsurface. In situ remediation case study reviews (Appendix E) have repeatedly found that injection programs are often under-designed with respect to the total volume injected. Therefore, high-level calculations of the total volume of fluids to be delivered should be performed as outlined in this section.

The basis for the calculations is the total volume of effective pore space in the TTZ. The effective pore volume (ePV) is calculated by multiplying the volume of the TTZ by the effective porosity. Effective porosity values can be estimated from the literature based on soil type or from site-specific predesign testing. When treating heterogeneous geology, the effective porosity of the treatment zone should be weighted based on the effective porosity of the high K (permeability) strata and the relative proportion of those strata unless the injection points will be installed such that screens do not intersect both high and low K zones. Using injection wells as an example, wells screened across a silt and sand layer will have the vast majority of flow through the sand. Therefore, the effective porosity relevant at the scale of the well screen would be calculated by the effective porosity of the sand times the proportion of the sand to the total well screen. Conversely, if nested well pairs are installed screened only in sand and only in silt, the effective porosity of the silt should be considered in the treatment zone effective porosity value.

The volume of fluid to be injected should be calculated in terms of fraction of the treatment zone ePV. For example, if an ePV is 100,000 gallons and the design specifies injection of 40,000 gallons, the design therefore specifies 0.4 ePVs. The fraction of an ePV to be injected can be thought of as the fraction of effective pore space in which groundwater will be physically replaced with reactive amendment—in the preceding example, 40%. Additionally, when less than 1.0 ePV is specified, the remaining pore space is (1) treated by ambient advection of amendment as a result of natural groundwater flow; (2) treated by diffusion of amendment; or (3) is not contacted by amendment (i.e., remains untreated). In our example, 60% of the treatment zone effective pore space would not be contacted by amendment as the result of initial injection but could be achieved through ambient advection as long as the amendment persists for the time it takes to achieve the design ROI. Limitations of injection of a relatively high percentage of ePV are identified in Table 3-3.

Table 3-3. Benefits and challenges of high ePV injections

Benefits of High ePV Injection	Challenges of High ePV Injection
Greater contact between amendment and target contaminants and less reliance on ambient advection and diffusion.	Increased time/cost associated with injection of a greater volume of fluid, possibly resulting in injection at higher flow rates that could fracture the TTZ.
More penetration of amendment into lower permeability material if amendment is persistent enough to allow for diffusion into low K zones.	Increased potential for displacement of impacted groundwater vertically (e.g., daylighting) and/or laterally outside the treatment zone.
Less reliance on diffusion or ambient advection of amendments. Critical to achieve overall ROI in low seepage velocity sites.	Increased potential for transport of amendments to unintended locations without hydraulic control. Achieving required treatment residence time in high seepage velocity sites.

The density of the injected fluid, if greater than that of the groundwater, can cause vertical migration of the injectate. Where there is a high degree of vertical stratification this may not be critical, but can cause the loss of amendment solution to zones deeper than the TTZ. If the injection fluid is less dense than the water (e.g., neat oils as carbon sources), there may be a buoyancy effect that again displaces the amendment into untargeted zones.

Multiple reviews of field-scale in situ remediation case studies have found that practitioners typically inject small volumes of fluids relative to the total pore space in the treatment zone (PERF 2013). (Suthersan 2017) determined that ISCO programs typically do not “inject adequate volume of chemical reagent to achieve sufficient distribution and contact” with target compounds. (Clayton 2007; Krembs 2010) found that 40% of ISCO case studies injected the equivalent of 0.01 ePVs or less (i.e., nearly half of the 27 case studies reviewed injected a volume less than 1% of the pore space in the treatment zone). (Krembs 2010) found that among sites where ISCO was used to treat PCE or TCE, the average number of ePVs injected was 0.5 for sites that achieved >90% reductions in target compounds (i.e., successful sites) versus an average of 0.24 ePVs at sites that achieved <90% reductions. This finding highlights the link between volume of fluids injected and the performance results attained.

3.5.3.2 Volume for Solid or Slurry Injection

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Injection of a solid by intentionally altering the subsurface permeability (i.e., fracturing) is fundamentally different from injection of amendment through existing pore space. When injecting solid amendments, the total volume delivered is generally a much lower percentage of the total volume of the TTZ. Rather than specifying the total volume of fluids to emplace relative to the total pore space (method outlined for injection above), solid or slurry injection-based programs are designed based on how far apart materials can be delivered from each fracture. (Appendix D5–Hydraulic Fracturing-Based Delivery Methods)

Once the injection details are defined (i.e., number of points and volume per point), it may be helpful to calculate the percent of ePV that is being proposed. The remainder of the treatment zone must then be contacted by diffusion or natural groundwater flow, which can be slow processes. For example, if a solid injection design results in injection of 0.02 ePVs, the design relies on diffusion and natural groundwater flow to treat the remaining 98% of the treatment zone (see the following section for additional discussion of advective distribution versus natural groundwater flow versus dispersion). The success of such a design depends on diffusion distances, groundwater flow rates and flow paths, and the persistence of the amendment in the subsurface.

3.5.4 Amendment Persistence

The persistence of an amendment is based on the reagents (individual chemicals or component) that are used to make up the amendment and the amendment dose. Some very soluble or aqueous amendments, and the resulting benefit or reactions generated by the amendments, may persist for days, weeks, or perhaps a few months, due to the reactions and processes that consume the amendments. As a result, additional amendment injection events may be necessary to sustain an effective treatment. Examples of soluble amendments include certain organic carbon substrates such as lactate, certain chemical oxidants such as hydrogen peroxide, or a pH buffering aqueous solution such as sodium hydroxide. Other amendments are insoluble or sparingly soluble, and after emplacement will slowly release (via dissolution, hydrolysis, or other processes) dissolved-phase amendments over a much longer period of time, ranging from months to years or potentially decades. As a result, a desired subsurface geochemical condition or treatment zone can be maintained for a much longer period of time without additional injection. Many types of amendments are available in both very soluble and more insoluble forms (for example, sodium permanganate [soluble] and potassium permanganate [less soluble]), which provides flexibility and optimization of remedial designs for site-specific conditions.

3.6 Amendment Delivery Optimization

There is typically a trade-off between the number and spacing of direct push points/injection wells and the volume of amendment injected per point or well. There will likely be constraints on the budget, injection pressure, site access, time for implementation, and available mixing and distribution logistics and equipment. This represents an optimization opportunity where the minimization of cost or time needed for the successful completion of the project is subject to those constraints. The optimization may initially consider the trade-off of cost vs. time (see Section 2.1.2) and/or certainty of successful treatment for different delivery strategies (e.g., inject and drift vs. recirculation) (see below). Optimization may be more applicable, however, to the refinement of the number and spacing of injection points, injection transects, and recirculation wells for minimization of cost or time using one of the delivery strategies.

There are advantages and disadvantages to both direct push injection and injection wells. Injection wells are often used if there is a plan to do multiple rounds of injection over time or if long-term amendment addition is planned, because once installed, there is less need for remobilization of the more expensive equipment such as drill rigs. However, there is less flexibility with injection wells compared with direct push points because the injections occur over the same depth interval at the same location for each round. If direct push injections are used, there is flexibility to target hot spots or areas of rebound or to target different areas or depth intervals on subsequent rounds of injections, and there is less chance of fouling of the screen interval that can occur with injection wells over time. Consideration must be given to the planned duration of injections, access constraints, maintenance requirements, and the expected need for flexibility in injection layout over time when determining which injection method is preferred.

The optimization analysis requires information on the unit costs and time necessary for all activities related to the injection project, including well installation or direct push injection, field labor, sampling and analysis, equipment rental, storage of amendments and equipment, etc. The analysis also requires estimates of the time necessary for transport or delivery of amendments into and through the subsurface, given the hydrogeology of the site. Modeling and pilot testing will provide information on these aspects. As previously discussed in Section 3.5, the behavior and persistence of the amendment once injected must be understood and estimated. See Figure 3-2 for four examples of amendment persistence under natural flow (see Section 3.8). Finally, the client’s time and budget constraints, as well as other site physical and access constraints, must be considered.

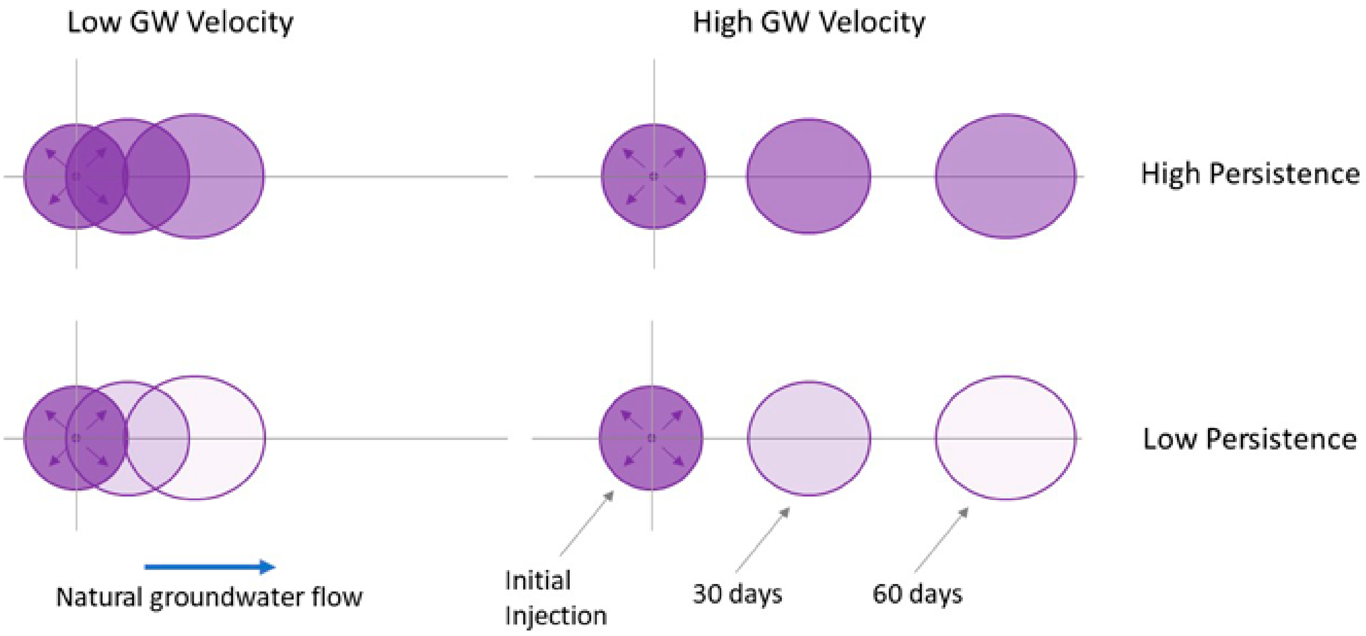

Figure 3-2. Amendment persistence at natural flow using four scenarios.

Source: Graphic used with permission from Trihydro Corporation.

Each example in Figure 3-2 shows a plan view of one injection point, with natural groundwater flow transporting the amendment away from the injection location. The distribution of the amendment is shown over time, with lighter shaded circles indicating that the amendment is depleted or less effective. In areas with low groundwater flow, the amendment will be depleted before it can be transported downgradient. In an environment with higher groundwater velocity, the amendment is distributed farther from the injection point before it loses effectiveness

With this optimization analysis information, the cost and treatment time for different injection point/line spacing can be estimated. The costs included in the analysis should include the added monitoring, labor, reporting, etc., that would be necessary for a longer remedy implementation period and not just the time needed for the amendment delivery. The combination of injection point, line spacing, and amendment volume per point with the minimum time or cost that meets the project constraints would be preferred. Some assessment of the uncertainty in the success of the implementation is necessary to allow for some factor of safety in the selected design. An optimal arrangement is usually one that is very close to violating one of the constraints, so some conservatism is needed in the selected design.

Optimization can also be applied to the determination of the TTZ, when multiple technologies are used in different portions of the site or at different times (see Section 3.2.3). The optimization can be done in a way to achieve the fastest or least expensive overall remediation through a trade-off between the boundaries or timing of the various applications.

Formal optimization tools, when used with models, can automate the process of constructing the relationships between design parameters and cost and time. (see Section 3.3.1 for more information on modeling)

The strategy of amendment delivery refers to the high-level approach that will be applied to the TTZ. For example, for a TTZ within a predominantly low permeability geology, injection rates should reflect the geology (e.g., lower flow rates with a control on the injection pressure) to prevent unintentional fracturing, short-circuiting, or daylighting. Considerations include the desired outcome (e.g., source treatment versus mitigation of off-site impacts) and the amendment distribution mechanisms that will be used during and after delivery. Several types of strategies are described below and in Figure 3-3.

- **Grid pattern**: Perhaps the most common method of delivery is to space delivery locations uniformly over the treatment zone and to deliver amendment at each of these locations. This approach is based on (relatively) uniform delivery of amendment away from each delivery location and does not intend to leverage postinjection processes, such as adjective flow, to distribute the amendment within the TTZ. This approach is the most broadly applicable, i.e., there are very few site-specific constraints that would challenge this method.
- **Inject and drift**: This strategy leverages distribution of amendment with natural groundwater flow (the advective phase). The spacing of delivery locations is greater in the direction parallel to groundwater flow. This method is applicable in situations in which the amendment is soluble in water, groundwater velocities are relatively high, and/or the amendment is relatively persistent in the subsurface.
- **Recirculation**: This strategy consists of simultaneous injection and extraction of groundwater. This strategy can increase the lateral extent of amendment influence and reduce the risk of daylighting of amendment. Use of this strategy is typically limited to sites with relatively high transmissivity. Extraction and reinjection of contaminated groundwater can pose regulatory challenges, though (USEPA 2000) clearly stated that addition of an amendment that will result in treatment meets the requirement that contaminated groundwater be treated even if that treatment occurs after reinjection.
- **Barrier**: This strategy consists of delivery in a linear transect such that contaminated groundwater flows into the treatment zone where it is treated. Such strategies use a barrier to contaminant migration, but not to groundwater flow. Barrier strategies are applicable to continuous delivery systems (e.g., ozone sparging) or to sorptive or insoluble amendments.

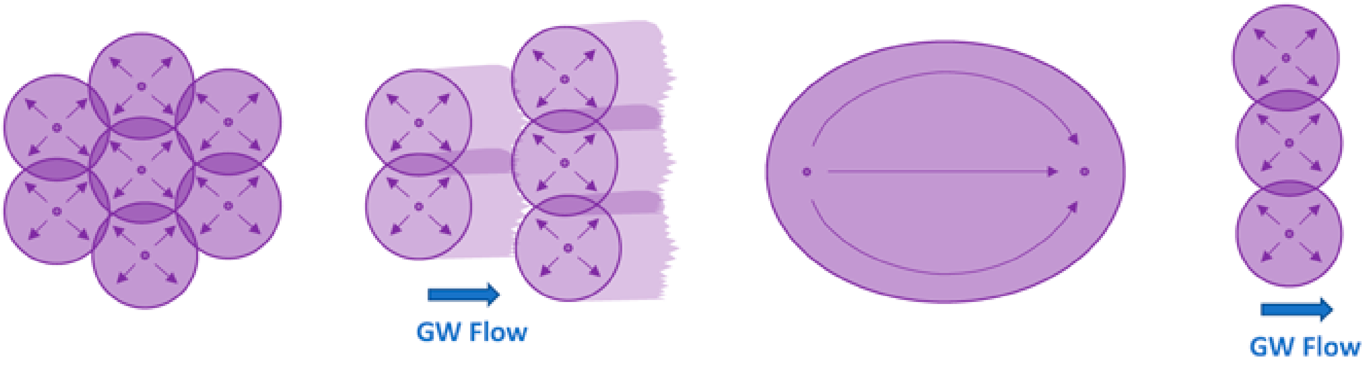

Figure 3-3. Plan view of amendment delivery strategies (from left to right: grid pattern; inject and drift; recirculation; and barrier). Note that these graphics are schematic depictions and are not to-scale; in general, ROI are not circular or smooth-edged but variable due to heterogeneities in the subsurface. Barrier strategies may typically require double rows of delivery points, and recirculation systems often use more than a single injection and extraction well. For high seepage–velocity sites, distribution is less circular and more elongated and the lateral, cross-gradient extent of ROI at the injection location may not be achieved.

Source: Graphic used with permission from Trihydro Corporation.

3.6.1 Overcoming Delivery Problems

Several factors can prevent optimal distribution of amendments. Poor estimates of required injection pressures or injection at higher than design rates to overcome poor distribution can prevent optimal amendment distribution or create preferential pathways, thereby not achieving uniform distribution in the TTZ. Fouling of the distribution pathways through biofouling, formation of inorganic precipitates, or gas build up reduces the permeability and can result in nonuniform distribution in the TTZ. Generally, fouling is a process in which a well screen, filter pack, and/or the surrounding formation become clogged over time. Fouling is most common for fixed injection wells, rather than direct push injection (DPI) (which can be repositioned if an area becomes fouled), especially if multiple injection events are required.

3.6.1.1 Injection Pressure versus Flow Rate

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A key relationship specific to injection-based technologies is injection pressure vs. flow rate. The injected amendment will displace groundwater already present in the effective porosity. This requires the application of pressure during the injection process to overcome the general resistance to fluid displacement. This can be exacerbated by a variety of factors, including the presence of confined or semiconfined layers, which will act as a roof or floor to the injection, preventing any upward or downward vertical groundwater displacement during the injection process. In these instances, it can be tempting to increase injection pressure to increase the injection flow rate; however, this creates a high risk of physically fracturing the matrix. If this happens, injection pressures will decrease, and injection flow rates will increase. Although this may have accomplished the desired outcome of increasing the rate of injection, many (or most) times this actually leads to delivery of the amendment to an unintended interval. Examples of this include surfacing of fluid during injection (daylighting) or delivery of the amendment to the vadose zone or other interval not intended for treatment (i.e., does not contain the targeted contaminants) (Appendix E.6, Oxidant Surface Eruption During Direct Push Injection). The recommendation is for precise control of injection flows and pressures to not exceed design distribution specifications throughout the entire injection process from flow initiation to ongoing injection.

Several different delivery strategies can be deployed to help overcome some of the physical limitations of injections. These strategies, which can decrease the unintentional risk of formation fracturing, are discussed in detail in Section 3.8.

3.6.1.2 Biofouling

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Biological fouling of wells can come in many forms, including slimes or biofilms, foams or pastes, and can accumulate on well screens, within the well filter pack, within the formation outside the filter pack, or on sampling and amendment delivery equipment. Biofilm production is a process in which bacteria adhere to a surface through a variety of natural forces and then reproduce to form colonies (ESTCP 2005b). The same processes that promote remediation also stimulate microbial growth and gas generation within the injection wells and remediation system infrastructure.

3.6.1.3 Fouling by Inorganic Precipitates

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The formation of inorganic precipitates can occur in the subsurface due to in situ treatment. Common changes in the subsurface resulting from a candidate treatment, which may induce inorganic fouling, may include, but not be limited to, oxidation-reduction potential, dissolved oxygen, pH, solubility, and sulfate concentration. Considerations to the potential changes can effectively be addressed and evaluated during the bench- and pilot-scale activities (Sections 3.3.2 and 3.3.3). If during pilot testing, scaling and precipitation of metals onto the well screen occurs, consideration should be given to using DPI over fixed wells for the full-scale remedy.

Other interactions with ions present in the groundwater and injected amendments may cause fouling over time. For example, the long-chain fatty acids derived from vegetable oil-based substrates may react with divalent ions such as calcium and magnesium dissolved in groundwater to form an insoluble precipitate in well screens and filter packs that is similar to soap scum.

3.6.1.4 Gas Fouling

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Fermentative gases generated from anaerobic microbial metabolic activities (for example carbon donor EISB applications) will occupy aquifer pore space and at least temporarily reduce hydraulic conductivity of the aquifer (Burnell 2013). These gases also create potential safety concerns as pressure backs up in fixed injection wells, such that the well cap could become a projectile. Buildup of aquifer gases also has the potential to yield erroneous water level readings, and it is important to vent monitoring wells before collecting or drill a vent hole to allow gases to escape. Further health and safety concerns associated with gas fouling of both injection wells and monitoring wells include the flammability of methane and the displacement of oxygen in the breathing zone.

3.6.2 Prevention and Control of Biofouling

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There are several strategies to prevent, limit, or control biofouling associated with EISB (ESTCP 2005b). Arguably the most effective stage for addressing biofouling is at the characterization and design phase, although physical and chemical well rehabilitation strategies are available after implementation. Although well rehabilitation using physical methods (e.g., scrubbing, surging, jetting), chemical methods (e.g., acid, chlorine) or other methods (heat, cold, ultrasound) are possible, the effectiveness is limited, they provide only transient improvement in well performance, and once fouling has started it can be difficult to control and rehabilitation will require repeated applications. A potentially more effective method of biofouling control is preventive biofouling controls such as the continuous or batch additions of chlorine dioxide, hydrogen peroxide, or other agents to prevent the formation of biofilms in the well screens (ESTCP 2005b). Selection of biofouling prevention agents needs to take into consideration the remedy and potential interferences from the biofouling agents (redox, toxic effects, etc.). Another option is batch dosing the amendment at high enough concentrations in the wells that the amendment concentration is toxic to the bacteria, and allowing natural gradient or the groundwater recirculation system to dilute the amendment out in the ROI.

Consideration should be given to using DPI points versus permanent wells and/or recirculation systems if biofouling is expected to be a significant concern see Section 3.6.2.1). There are many pros and cons of using direct push technology (DPT) versus wells for injection of amendments that are addressed further in Section 3.8, Delivery Strategies, but one of the advantages is that a DPI point is usually temporary enough that no biofouling will occur around it.

3.6.2.1 Design Considerations

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Prevention of biofouling in wells used in delivery or monitoring is achieved by having a solid understanding of hydrogeology and contaminant distribution. Major factors to consider at the design stage that are likely to cause future fouling problems include total organic carbon, metallic cations, phosphorus, nitrogen, and the integrity of the surface seal to withstand injection pressures (USACE 2003). A thorough site characterization is also essential for limiting amendment volumes so that the site-specific electron donor demand is met and not exceeded (ESTCP 2010b). In doing so, monitoring wells are less likely to be influenced by microbial growth or the amendments themselves. Design-based characterization is discussed in Section 2 of this document. Because biofouling is often observed during EISB, remedial plans should include a well monitoring and maintenance plan to identify the occurrence and mitigation strategy of biofouling. Such a plan may include both physical and chemical well and infrastructure rehabilitation methods. Flushing the injection lines and well screens after substrate injection for EISB will reduce amendments in the wells and help to minimize biofouling or separation of products such as emulsified vegetable oil (Appendix D6–Pneumatic Fracturing-Based Delivery Methods).

3.6.2.2 Operational Strategies

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Both performance monitoring and the rehabilitation process can be used to minimize fouling. Injection wells should be monitored periodically for wellhead pressures, depth to water, static water levels, injection flow rates, and volumes so that any losses in injection capacity are quickly identified. Visual inspection of the well screen (e.g., downhole camera) is also valuable for identifying the presence and severity of biofouling in both injection and monitoring wells. The frequency of monitoring events should be designed such that fouling issues are recognized quickly and can be mitigated. Various operational strategies can be used, including:

- flushing wells postinjection of electron donors
- mechanical well rehabilitation
- chemical well rehabilitation

Well rehabilitation methods are described in A Review of Biofouling Controls for Enhanced In situ Bioremediation of

Groundwater, October 2005.

3.7 Delivery Layout Design and Volume per Location

This section describes the methods for determining the number of delivery locations, their spacing, and how much volume to deliver at each location. The text in this section assumes that the following data have already been generated: RDC data (see Section 2); the preferred amendment type and general delivery method that emerged from screening (see Section 3.4); the definition of the TTZ (see Section 3.2.1); the mass of amendment required (see Section 3.5); the strategy for amendment delivery (see Section 3.6); and the overall volume of fluid to be delivered (see Section 3.5.3).

The number and spacing of injection locations should be based on the overall goal of achieving adequate distribution of amendment throughout the TTZ. Amendment will travel through the subsurface through the following processes subject to the constraints listed below.

- **Advection as the result of pressurized delivery**, i.e., physical displacement of pore water (for injection) or formation of new porosity as the result of fracturing (for emplacement). The primary constraints on advection during delivery are: (1) preferential flow through higher permeability zone, and (2) limitations on the volume injected and amount of time allotted for delivery. Transport of many amendments will be greatest during active injection.
- **Advection due to natural groundwater flow,** which can transport amendments additional distances after active delivery ceases. Constraints on ambient advection are: (1) the rate at which the amendment is depleted in the subsurface, (2) the propensity of the amendment to move with the groundwater or adhere to soil surfaces, and (3) preferential flow through higher permeability zones. The choice of the amendment will also impact the distribution. Soluble substrates should distribute farther than fine particles of emulsified vegetable oil (EVO) or large-scale particles of ZVI. The nature of the amendment will also impact transport, with nonionic particles less likely to react with charged soil particles than charged amendment particles.
- **Diffusion as the result of concentration gradients,** which is constrained by (1) amendment depletion in the subsurface, and (2) slow rates of diffusion.

3.7.1 Number of Delivery Locations and Volume for Injection of Liquids

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The process of defining the number of delivery locations and the volume to be delivered at each location is typically an iterative process. For simplicity, this section assumes that delivery at each point will be the same, i.e., same volume and same intended ROI. In reality this is not always true as variations in geology and hydrology may vary within a few feet. The amendment is delivered at specific locations and travels outward from these locations, ideally throughout the rest of the TTZ. Determination of the number and specific locations for delivery of amendments is based on an assessment of how far the amendment will go (ROI), which is in turn a function of how much volume is delivered.

3.7.1.1 Desired Radius of Influence

The first step is to determine the desired ROI. The term “ROI” can be misleading because it implies uniform distribution in each lateral direction and at each depth. In the design of the pilot study and/or field implementation of a remedy, the ROI can vary vertically as well as laterally. Appropriate consideration should be given to adequately plan an effective pilot study/remedy by using ranges of ROI. Geologic heterogeneity results in preferential flow through higher permeability zones. Unconsolidated (sedimentary) geologic deposits are stratified vertically, thus preferential flow occurs as a function of depth. This is shown graphically in Figure 3-4. Both panes show delivery of approximately 0.1 ePVs of amendment. The less heterogeneous case (left) results in delivery of amendment in the vicinity of each of the delivery points. The more heterogeneous case (right) results in substantial variability in lateral influence versus depth. Figure 3-4 shows photographs of heterogeneous and homogenous dye delivery (Clayton 2008).

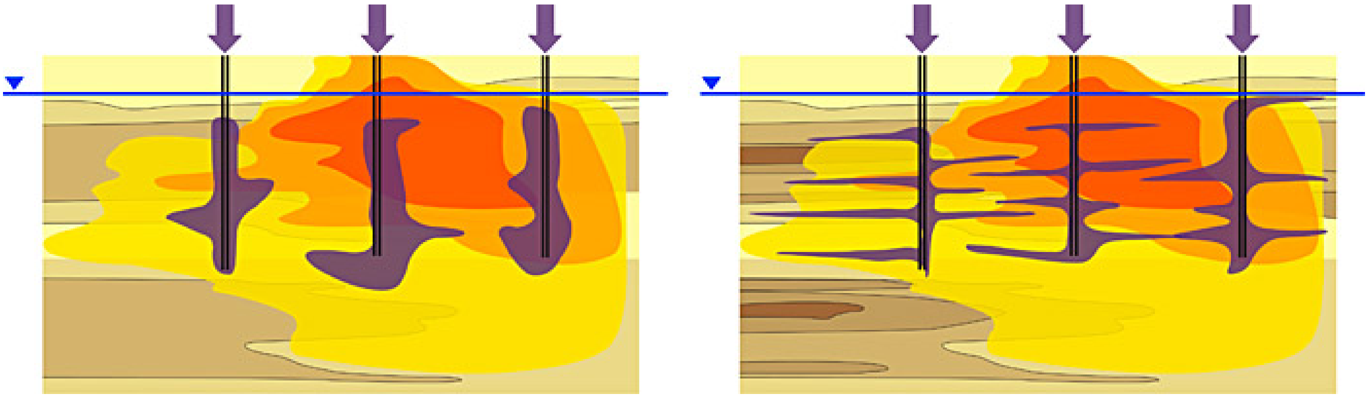

Figure 3-4. Cross section view of heterogeneous oxidant transport (graphic used by permission from Trihydro Corporation, modified from (Clayton 2008) presentation "*In situ* Chemical Oxidation (Basics, Theory, Design and Application)" presentation to California DTSC Remediation Technology Symposium, May 14-16.

Source: Photographs by W. Clayton, Trihydro. Used with permission.

Photographs of heterogeneous and homogenous delivery are shown in Figure 3-5, including heterogeneous delivery of dye tracer with lateral direction from injection points (left, picture taken looking down into pit) and relatively homogeneous permanganate distribution in a sand as a function of depth (right, picture taken after soil cores have been removed from subsurface, showing the permanganate distribution at various injection depths).

Figure 3-5. Heterogeneous and homogenous delivery of dye tracer.
Left image shows heterogeneous delivery of dye tracer with lateral direction from injection points (picture taken looking down into pit). Right image shows relatively homogeneous permanganate distribution in a sand as a function of depth (picture taken after soil cores have been removed from subsurface, showing the permanganate distribution at various injection depths). Photographs by E. Cooper, Cascade Environmental, used with permission.

Once the desired ROI has been determined, the next step is to assess how injection should be designed to attain this ROI. If a pilot study has been performed, the site-specific data generated should be used in this assessment (see Section 3.3.3). However, heterogeneous geologic conditions invariably result in some amount of preferential flow as a function of depth and radial direction. The equation for the volume of a cylinder (V= $\pi*r^2*h$) is nevertheless a starting point in evaluating the relationship between injection volume and how far the amendment might travel laterally during delivery (see Section 3.5.3.1). Modeling tools can also be applied during this assessment (see Section 3.3.1). Practitioner experience can be brought to bear, but with some caution. Experience at other sites is applicable only to the degree that the subsurface conditions at the other sites are similar to the site in question. Additionally, just because a practitioner used an approach at other sites does not necessarily mean that those other sites were successful.

The desired ROI is often influenced by the dimensions of the TTZ. For example, if a plume is 3 m wide, a lateral influence in the range of 1.5–2 m should allow treatment of the entire width of the plume. For this 3-m wide plume, a lateral influence of 3 m would result in substantial delivery of amendment beyond the limits of the plume. A lateral influence of 1.2 m or less would require multiple delivery points per row to treat the entire width of the plume. Additionally, surface or subsurface features may dictate the distance of influence as well. The assumption is that all delivery points are straight and completely vertical. Rocks and other heterogeneities can deflect the delivery point into unintended directions.

Once the lateral ROI and injection/emplacement volume are specified and the ROI is determined, these data are scaled up across the treatment zone. How this is done depends on the strategy. For grid patterns, the delivery locations and ROI are overlain on a map of the TTZ. For inject and drift, spacing between points in a given transect is based on the ROI. The spacing between transects is the sum of the ROI plus the distance amendment will travel during drift, which is estimated by groundwater seepage velocities and the rate at which amendment will be consumed. For barrier applications the spacing within transects depends on the ROI. Groundwater velocity and ROI should be used to estimate groundwater residence time in the barrier treatment zone. The groundwater residence time is usually estimated using the hydraulic conductivity and the gradient. The residence time can be increased by adding a second offset and parallel transect of injection locations, to ensure there are no dead spots in the barrier that would let contaminants through. Multiple barriers across the site will likely be required for large plumes (Appendix E.13, Former Industrial Site Characterization and Remediation in Fractured Rock), and/or plumes with slow groundwater flow rates.

When specifying the number and spacing of delivery locations, and the volume to be delivered at each, the following should be considered.

- Use of a greater number of more closely spaced points will result in more reliable distribution, all else being equal.
- Injection of a greater volume at each point results in greater distribution away from each point. However, there is a practical limit to how much volume can be injected. Preferential flow through higher permeability zones can result in repeatedly treating high permeability zones or excursions of amendment outside the TTZ when high volumes are injected.

To overcome vertical stratification of amendment at heterogeneous sites, most often after adequate high-resolution characterization has been performed to identify these intervals, several methods can be used.

- Direct push points with delivery performed at discrete (e.g., 0.3 m or 0.6 m) zones can force more uniform distribution, assuming equal volumes are injected at each depth. Note that in heterogeneous formations, the delivery pressure, or time allotted, will be highly variable at different depths when using this approach.
- Injection wells with shorter screens can be used with nested wells when the TTZ is relatively thick.
- Where soluble amendments are to be delivered into a plume of dissolved contaminants generally created by advective flow, the use of a recirculation system can more widely and rapidly deliver the amendment. The recirculation system consists of paired extraction and injection wells, a treatment/amendment addition system, and associated piping. It is used to extract groundwater, possibly treat it if necessary, amend the water with compounds suitable for the desired in situ treatment process, and inject the solution into the subsurface. The locations on the extraction and injection wells are chosen to strategically distribute the amended water in an optimal fashion while controlling the plume.
- The paired extraction and injection increase the hydraulic gradient, and this speeds the travel of the amendment relative to the natural gradient. In addition, the nature of the flow paths for water traveling from an injection to a paired extraction well expand outward before converging on the extraction well. This results in a generally better lateral distribution of amendment. Overall, the use of paired extraction and injection serves to increase the well spacing and reduce the number of injection points. This offsets at least part of the capital cost for the extraction system.
- If 3-dimensional heterogeneity is relatively well known (e.g., via hydraulic tomography (ITRC 2015)), targeted, and perhaps multiple, simultaneous injection and extraction points, and multiple packed-off zones, could be used

for pumping/injection flow control to guide injection to desired volumes.
- Phytoremediation systems can be used to influence hydraulic control. They perform in a manner similar to extraction wells, without the need for recirculation. The coupling of in situ injection strategies with phytoremediation is best used in conjunction with aerobic or oxidizing amendments in areas where the hydraulic conductivity is low. Phytoremediation may also offer a polishing step or can be used in transects parallel to injection transects./li>

3.7.2 Number of Delivery Locations and Volume for Injection of Slurries/Solids

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When delivering amendments, the number of points and their spacing depend on how far the amendment will travel from the point of injection. Similar to injection of liquids, the spacing depends on selecting a target ROI and then determining how to perform the injection such that the target ROI is achieved. Because the injection of slurries/solids is nearly always performed by specialized contractors, such contractors should be consulted to determine the required delivery parameters. Alternatively (or in conjunction with), the ROI can be assessed with a site-specific pilot test.

Amendment distribution is extremely stratified with depth when materials are injected into fractures. The fractures themselves contain amendments in the concentration that were injected, while the remainder of the subsurface may not receive any amendment during the initial emplacement. Where fractures are parallel to groundwater flow (i.e., horizontal fractures and approximately horizontal groundwater flow), natural groundwater flow will likely not cause contaminants to intersect the emplaced amendment. In these cases, diffusion is the primary mechanism through which amendments are delivered to contaminants away from the fractures (Siegrist 2001) or contaminants into the amendment in the fractures (ITRC 2017a, b). A detailed study of permanganate transport away from fractures found that permanganate diffused approximately 0.3 m outward from fractures in each direction in approximately one year (Siegrist 2001).

3.8 Delivery Strategies

Whether via permanent, fixed points or temporary locations, amendment distribution through a porous aquifer media is controlled by the nature of the amendment (soluble, semisoluble, or insoluble), the permeability of the formation, the volume of amendment added, and the pressure at which the fluid is applied to the formation.

Advection-dominated transport controls the flow of groundwater, contaminants, and amendments. These high permeability zones often receive the most fluids, allow broadest radial delivery, and are therefore key to determining injection location spacing. As a result, these zones are often where the most rapid and extensive treatment gains can be achieved. Advection-dominated transport includes rock and soils with large hydraulic conductivity values (fractured limestones, gravels, sands), but can also zones of moderate relative permeability (silty sands, clayey sands) with slower rates of advection compared to storage zones dominated by diffusion (see Section 3.5.3.1). To avoid driving contamination outside the treatment area, it may be advantageous to begin injection near the fringe of the plume/aqueous phase and progress upgradient where multiple injections are required.

A variety of amendments are available to promote biological or chemical transformation, depending on the properties of a specific target contaminant. These amendments all have different chemical properties that control their introduction and transport through the subsurface and potentially limit the injection methods available. The particle size of many solid-phase amendments such as oxygen-releasing materials, ZVI, or activated carbon is larger than most pore throats and prevents delivery through well screens. High-pressure emplacement technologies using hydraulic or pneumatic methods are therefore required to deform the aquifer matrix and propagate seams (fractures) within the aquifer matrix. Conversely, soluble amendments like organic carbon substrates and chemical oxidants can be delivered under gravity flow or at low pressure via permanent or temporary well screens and via high-pressure fracturing methods.

Given that natural aquifer conditions control both contaminant and amendment transport, mapping the contaminant distribution within the aquifer architecture is key to determining what delivery approach to select. Wells and fracture-based injection points can both be successfully used for delivery through more permeable advective soils, but the applicability of injection wells declines as the matrix become less permeable. To address contaminants residing in lower hydraulic conductivity zones, fracturing technologies are used to propagate amendments at the desired target depth. In these cases, fractures are established to serve as new zones of higher permeability within the rock matrix. Amendments with greater longevity emplaced within these fractures can diffuse into lower permeability soils adjacent to the fracture and provide treatment of contaminants migrating from the low permeability zones into the new fracture interval.

Finally, injection method selection is determined based on site access constraints and remedial goals. For sites where only one injection or emplacement event is planned, or where the installation of permanent injection wells is infeasible, temporary injection points and emplacement-based methods are often preferred. When multiple injection events are expected and the rock matrix is more permeable or conducive to well-based delivery, it is often more economical to install permanent injection wells to reduce overall project life cycle cost.

3.8.1 Injection Screening Matrix

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The injection/screening matrix (Table 3-4) features six delivery methods as column headers. Along the far-left column is a list of subsurface characteristics that influence the applicability of the injection methods. The cells of the table contain one of three parameters/terms:

“Widely used = ●”, “Site-specific = ▣”, and “Not applicable = NA”

Select the hydrogeologic or physical characteristics that best fit the site-specific TTZ of injection (targeted mass or groundwater zone). The selected row/cells will indicate the general feasibility of the various delivery technologies. For example, nearly all the delivery technologies can be “widely used” for very coarse sands (sandy to gravelly) except for electrokinetics, which is site-specific.

When one or more delivery technologies have been selected for the TTZ based on its characteristics and/or conditions at the site, the next step is to click on the appropriate column header to link to specific fact sheets. Each fact sheet discusses four topics:

- types of equipment
- types of delivery
- advantages of this delivery technique
- limitations to this delivery technique

As noted in Table 3-4, Solid Injection Principles [D4] appears as a master header over Hydraulic Delivery and Pneumatic Delivery to present an understanding of these two delivery methods for injecting solid amendments.

Table 3-4. Injection screening matrix.
“Widely used = ●”, “Site-specific = ▣”, and “Not applicable = NA”

Delivery Technique	**Direct Push Injection (DPI) [D1]**	**Injection Through Wells & Boreholes [D2]**	**Electrokinetics This is injection through wells. [D3]**	**Solid Injection [D4]**		**Permeable Reactive Barriers (PRBs) [D7]**
Hydrogeologic Characteristics Unified Soil Classification System				**Hydraulic Delivery Through Wells & Boreholes [D5]**	**Pneumatic Delivery Through Open Boreholes [D6]**	
Gravels	● (Sonic)	●	NA	NA	NA	●
Cobbles	● (Sonic)	●	NA	NA	NA	●
Sandy Soils (Sm, Sc, Sp, Sw)	●	●	NA	▣	▣	●
Silty Soils (Ml, Mh)	●	▣	●	●	●	●
Clayey Soils (Cl, Ch, Oh)	●	▣	●	●	●	●
Weathered Bedrock	●	●	▣	●	●	▣

Delivery Technique				**Solid Injection [D4]**		
Hydrogeologic Characteristics Unified Soil Classification System	**Direct Push Injection (DPI) [D1]**	**Injection Through Wells & Boreholes [D2]**	**Electrokinetics This is injection through wells. [D3]**	**Hydraulic Delivery Through Wells & Boreholes [D5]**	**Pneumatic Delivery Through Open Boreholes [D6]**	**Permeable Reactive Barriers (PRBs) [D7]**
Competent/Fractured Bedrock	NA	●	NA	▣	▣	▣
K ≤ 10^{-3} to 10^{-4} (Low Perm Soils)	●	▣	●	●	●	●
K ≥ 10^{-3} (High Perm Soils)	●	●	▣	▣	▣	●
Depth > Direct Push Capabilities	NA	●	▣	▣	▣	▣

3.8.2 Material Compatibility and Other Safety Considerations

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When making delivery equipment decisions, the primary concern is how the reagents will react with the materials of construction in some way, possibly compromising the integrity of either the reagent or the equipment parts (hoses, fittings, seals, pipes, etc.) that come into contact with the amendment. Reviewing Safety Data Sheets (SDS) for the amendment compatibility is important to understand each component’s specific chemical and physical properties. In addition, the compatibility of the reagents/amendments should be considered with the specific types of plastics, grades of steel, types of O-rings of all of the equipment, conveyance infrastructure, and well materials anticipated to contact the amendment. Injection contractors can provide detailed information regarding their equipment and its compatibility with different amendments. The sequence and timing of mixing solutions that will initiate reactions (e.g., the reaction between catalysts and oxidants) should be discussed in detail with the manufacturer and the injection contractor to mitigate adverse material compatibility. Some materials result in corrosive or exothermic reactions when combined (e.g., sodium persulfate or hydrogen peroxide and iron activators).

Other safety precautions to consider include checking the age and condition of tooling, pump tightness testing that is a water test in the field prior to initiating reagent injections), installing adequately sized whip-checks at pressurized connections, and securing an adequate exclusion work space or buffer zone within the line of fire protection. These are a few safety concerns and are not meant to serve as an exhaustive list of potential safety issues.

Both ionic and nonionic species can be mobilized through the formation via different electrokinetic processes (Factsheet D3). Compatible reagents include a wide array of oxidants, pH buffers, salts, and catalytic reagents.

3.8.3 Implementation

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When the user has selected the amendments and confirmed that the delivery technique is compatible with both the target zone subsurface conditions and equipment for that delivery, the user is ready to proceed to Section 4, Implementation and Feedback (Monitoring) Optimization.

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4 Implementation and Feedback (MONITORING) Optimization

This section addresses site-specific logistical and permitting issues that should be considered before mobilizing to the site as well as during implementation optimization of the remedy to include changes to dose, amendment, and delivery (see Section 1.3). The remedy may be optimized at any stage based on the evaluation of monitoring data.

4.1 Pre-implementation Considerations

Health and safety plans (HASP) and procedures developed during predesign activities should be reviewed and updated prior to field mobilization to protect the health and safety of site workers and the surrounding community. Changes and improvements in safety procedures developed during predesign site characterization, bench testing, and pilot testing should be incorporated before and during optimization of the remedy. In addition to drilling and subsurface utility hazards, in situ remediation also presents some unique health and safety considerations for the injection of reagents and substrates. These include hazards associated with the chemical amendments themselves, application hazards such as increased subsurface pressures or temperatures, reagents surfacing, and post application hazards such as increased byproduct concentrations, metals mobilization, or vapor intrusion (NAVFAC 2013a). Proper engineering controls for these hazards should be identified and included in the HASP (e.g., USEPA Underground Injection Control Regulations)

Pre-implementation considerations also include federal, state, and local regulatory and permitting requirements associated with the implementation and modification of in situ remedies. Inconsistencies between various federal and state programs can present regulatory challenges. As discussed further in Sections 5 and 6, early communication with the relevant regulatory agencies and stakeholders, early start-up on the HASP development, and an understanding of the necessary permitting requirements are critical to facilitate timely regulatory and stakeholder acceptance.

4.2 Adaptive Implementation and Feedback Optimization

Remedy design is an iterative process that unites consideration of site characteristics, amendments, and delivery method. It is important to recognize these truths:

- The data set for a site upon which to develop a CSM and corresponding design will never be perfect or fully complete.
- Factors that influence design cross many orders of magnitude in scale, from the molecular to the site-wide level.
- Site conditions change at time frames that range from minutes to decades.
- Although our models and designs often assume homogeneity, heterogeneity is the rule.
- Amendment transport in the subsurface is (to a first order) dependent upon the site geology, hydrogeology, and delivery method, but nonetheless often seems random and chaotic due to the smaller scale heterogeneities.

It is therefore important to integrate mechanisms for process monitoring, feedback, and flexibility during implementation into the remedial design process.

4.3 Implementation and Optimization Staircase

To conceptualize the iterative process, the design wheel and optimization staircase (see Section 3.1) were developed. Note that in some cases, the results of a bench-scale or pilot test may lead to another bench-scale and/or pilot test before moving into full scale. Optimization is not meant to create an endless cycle of testing and project delays, but to create a remediation strategy that is cost-effective and efficient by targeting the contaminants in the most effective manner. Once the project goes to full scale, this approach is commonly used for subsequent planned injection events, and the monitoring data dictate where and when the next injections will be needed. This approach may not be critical for small, well-understood plumes, but can save millions of dollars and decades of time when the optimization staircase is applied to large, complex plumes (see Section 2.1). At all stages of data collection, consider the cost of collecting analytical data versus the benefit. Also consider the implications of not collecting data, which could result in long-term cost avoidance if properly evaluated.

Within the staircase, there are opportunities to make minimal adjustments to the full-scale remedy. These may be minor adjustments to the remedy that require the practitioner to step back to the pilot study (or bench-scale position if the change is recommended during the pilot study) or make major changes to the remedy that also require return to the bench-scale test. Such decisions are based on a review of the monitoring data and professional judgement. Minimal changes include changes to volume of amendment added, changes in the number of injection points, increasing or decreasing amendment dilution, addition of buffers or bioaugmentation of bioremediation systems, or change in the activator for chemical remedies. Although these changes are considered minimal, some states will require updates to the underground injection control (UIC) permit. Changes that include alterations to the amendment for which stepping back to additional pilot testing is required will likely result in a change to the UIC permit. Major changes, such as moving from bioremediation to chemical oxidation or chemical reduction, may require additional bench-scale testing and may require changes to the decision documents.

4.4 Monitoring

For the purposes of this document, monitoring involves process monitoring and performance monitoring. Multiple lines of evidence are helpful to sufficiently demonstrate that in situ remedies are functioning as designed (Section 4.4.2.3). Therefore, both process and performance monitoring are critical.

- Process monitoring provides an understanding of the operation of the system prior to injection (aboveground), and the postinjection hydraulics, and/or the immediate chemical effect (underground). It also includes the collection and interpretation of monitoring data that provide information on the state of the remedial action during implementation.
- Performance monitoring relates to the collection of monitoring data that provide information on the potential success of the remedial action to achieve remedial goals. It also includes compliance monitoring.

A process and performance monitoring program may involve collection of similar data, and these monitoring plans may be grouped into a single document at some sites; however, the timing of data collection events and the actions taken as a result of the data obtained differ.

4.4.1 Process Monitoring

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Process monitoring for start-up activities typically involves confirmation that pumps, mixers, blowers, compressors, and other mechanical equipment are operating within the expected ranges as each is exercised for the first-time during operation. (System shakedown is assumed to already have been performed to troubleshoot construction issues, and all equipment should be able to operate as designed at this stage.) If amendment mixing is part of the operation, the volumes of water and materials to be mixed should be confirmed through both measurements and estimates of flows or material quantities. Dosage pumps, flow meters, and flow totalizers are often used to control and measure amendment dose. Direct measurement of amendment concentration using field kits, which is verified by samples collected for laboratory analysis, provide further monitoring of the process.

Monitoring of injection hydraulics includes measurement of flow rates and pressures and may include evaluation of changes in groundwater elevation across an injection network and the observation of tracers, or amendments, at observation wells within or at the fringes of the TTZ to confirm hydraulic performance. If a significant number of monitoring points will be used, or monitoring will extend over a significant period, data logging devices or telemetry may be used to capture and preserve the data for further analysis. Groundwater chemistry effects may include changes in pH and other geochemical conditions, the arrival of amendment at a monitoring point at a desired concentration, or evidence of the intended reactions or secondary affects to be avoided, such as mobilization of chemicals of concern or increased metals solubility.

The data collected should be benchmarked against design and cost estimate assumptions to confirm that the target area was influenced, the emplacement of amendments occurred at the target concentrations, the geochemical effects needed to facilitate treatment (such as pH modification) were achieved to the extent needed, the timing of injection was consistent with expectations at the flow rates and pressures observed, and systems used to perform treatment operated as expected. If these fundamental objectives were not achieved, modification to the treatment approach, system design or operation, volumes of amendment, concentrations of amendment, or other factors may be needed.

4.4.1.1 Process Monitoring Design Considerations

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Process monitoring of in situ remediation at pilot- and full scale represents a set of activities that must be carefully planned, designed, and executed to help ensure desirable contaminant reduction or stabilization outcomes in the face of complexity and uncertainty commonly associated with the subsurface stratigraphy, contaminant presence, contaminant migration, and remedial performance. In the context of this guidance, process monitoring is defined as the observation and documentation of remedial equipment performance used to affect changes and subsequent response of the TTZ and surroundings. Perturbation of the TTZ pore pressure, temperature, fluid viscosity, geochemistry and microbial populations, and changes to solid surfaces biogeochemistry, effective stress, permeability, and other basic and derivative properties and features can be anticipated by the act of injecting fluids and emplacing solids (colloids, particles in slurry form), collectively referred to as *amendment*.

The design for process monitoring should seek to address key features and questions concerning the specific remedial technology that is to be piloted or deployed at full scale and the site-specific subsurface hydrogeology, geology, biogeochemistry, and contaminant distribution and fate under natural and induced conditions. Additionally, project constraints related to budget, schedule, resource limitations, and safety must be observed to arrive at a process monitoring design that is balanced technically and otherwise. Sources of information that could represent starting inputs to the design of process monitoring programs include the RDC, analytic and numerical modeling, treatment amendment vendor-supplied information, bench-scale treatability testing, and results from field and laboratory testing recently performed to fill pressing data gaps not yet integrated into the RDC. Information from other sites of a similar nature to the subject site can be valuable. Numerous public and private guidance documents are available that provide best practices and other information that can assist in design of an effective process monitoring program (NJDEP 2017; USEPA 2018b); (Neilsen 1991).

Within the design stage, basic details and options associated with process monitoring, as well as performance assessment monitoring, should be outlined in a preliminary manner when the core attributes of the remedial technology application have been defined. Attributes of process monitoring that are typically considered, and often specified, during the design process for injection-based groundwater treatment remedial approaches are listed below:

- baseline (see Section 4.4.2.3) aqueous geochemistry and/or microbial population characteristics within the TTZ and upgradient and, potentially, side-gradient (background)
- baseline biogeochemical characteristics of the sediment/soil or bedrock within the TTZ (background)
- amendment quality assurance characteristics, e.g. pH, DO, ORP, viscosity, constituent concentration, particle size, stability/variability of liquid mixtures (e.g. ZVI and EVO, other parameters) at time of materials delivery acceptance, mixing preparations, and/or subsequent storage prior to use
- injection pressure and flow rate at critical location(s) within mixing and injection equipment subsystems such as at manifold locations, pressure relief valves, and individual injection borings or wellheads
- total volume of amendment delivered to individual boreholes or wells. Note that flow meters are usually accurate +/–3% and must be positioned per manufacturers' recommendations within the injection system. Also, if magnetic flow meters are not used for solids flow measurement, the accuracy of measuring volume reduction in feed tanks should be considered.
- subsurface hydraulic response to injection (e.g. tilt meters or surveyed ground surface elevation changes), including intentional and inadvertent formation fracturing and subsequent emplacement of solid treatment amendments and permeability enhancement components (propping agents)
- subsurface volume within which aqueous- and/or solid-phase biogeochemistry is altered by direct and indirect action of injection
- specific chemical, physical, and microbial responses (e.g. pH, DO, ORP, TOC, sulfate reduction) within and around the TTZ that, taken individually or in unison, provide lines of evidence for assessing the degree of success or failure in achieving desired injectate amendment constituent (or injectate amendment constituent byproduct) reactions and, by extension, COC treatment outcomes.

Prior to mobilizing for pilot- or full-scale implementation, baseline conditions in and around the TTZ are established to provide a context for interpreting the process monitoring data. Proper documentation and timely interpretation of the process monitoring data, and its subsequent use, are critical aspects of optimization. The data obtained from the process monitoring effort can be divided into two categories, one being physical responses and the other chemical/biogeochemical responses. With respect to the latter, focusing on chemical and biogeochemical changes helps to verify that in situ treatment is developing or progressing as intended (or not). Specific questions that are addressable with an effective process monitoring program include:

Where did the amendment go? Soil borings, discreet groundwater samples, or EC logging may be necessary to identify the ROI of certain amendments.

- Are (or did) the injectate amendment constituents performing their intended role?
- What are the immediate chemical/biogeochemical and COC response trends?
- Are physical changes, such as permeability reduction or increase, occurring that provide clues as to chemical/biogeochemical response?
- Are there indications of problems or unexpected outcomes now or forthcoming?
- Are there opportunities for optimization of the treatment details, process monitoring, or both?

Ultimately, it is necessary to assess not only the short-term effectiveness of the implementation but also the longer term practicality of the strategy and technology being applied. If short-term effectiveness appears to be lagging, are there discrete optimization activities that can put the remedial action on the desired path? Is a more dramatic change in technology, such as amendment delivery technology, warranted by the process monitoring data? Refer to the optimization staircase (see to Section 3.1) as these questions are asked and answered.

4.4.1.2 Process Monitoring Implementation

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The process monitoring stage should focus on collecting data to confirm that the amendments are introduced and distributed according to the design, and that the application method is appropriate. The types of questions that a practitioner should be asking when reviewing the process monitoring data include:

- Are injection pressures and flow rates consistent with design expectations? If pressures and flow rates are very different than expected this may indicate that the subsurface geology is different than that for which the system was designed.
- Is the amendment being delivered where and how it was designed to be distributed?
- Is the design volume of amendments injected as expected at all locations? What is the strategy for locations or intervals that were lower or missed altogether?
- Are unusual results (for example, indicator parameters/analyses, water level changes, etc.) occurring at nearby monitoring wells?
- Is daylighting or breakthrough observed at utility corridors, drainage channels, surface water features, or monitoring wells that are far from the injection area where breakthrough was not expected?
- Do the indicator parameters support that chemical or biological reactions are occurring as expected? For example, were unusual temperature changes, pH, ORP, DO, vapors, color changes, or other physical changes observed during injection?
- If data are not as expected, are corrections possible during the ongoing field event? What is the communication plan for reporting results in real-time and who is the decision maker for implementing changes? (see Section 4.6.2 for additional discussion of contingency plans)

4.4.1.3 Process Optimization

Process monitoring data should be evaluated in real time, or as close to real time as possible to allow in-field adjustments (optimization) to be made. Because of the real-time aspect of process monitoring, it is essential that experienced field staff be involved in the implementation of the process monitoring plan, and that all staff involved in the remedy implementation are appropriately trained and are aware of the remedy objectives, expected results, and triggers for actions. A comprehensive work plan or field implementation plan should anticipate potential complications in the field and provide a contingency for likely scenarios.

A formal, centralized process should be established to manage and communicate changes made to the original implementation plan as a result of the process monitoring data. Suggestions for this communication pathway are given in (ITRC 2011d). Changes should not be made in isolation, as a change in one area of the implementation methodology may have follow-on effects. The potential impact of that change on future process monitoring data evaluations should be considered and incorporated throughout the optimization process (see Section 4.3).

Table 4-1 provides some examples of observations that may be made during the course of process monitoring, and potential implications. Table 4-1 should not be considered an exhaustive list and there are many site-specific factors that contribute to interpretation of the data. This table represents a few common observations and potential failure mechanisms to be aware of.

Table 4-1 ▼*Read more*

Table 4-1. Typical observations during process monitoring.

Data Type	**Scenario**	**Potential Implication**
Water Level	Water levels at nearby monitoring wells (e.g., 3 m) show a significant increase with very little fluid injected into the injection well location.	This type of result may indicate a connection or preferential pathway. Be aware of the potential for daylighting and for amendment distribution challenges.
Pressure	Injection pressures are higher than expected.	Tight soils or biofouling (Section 3.6.1.2) may be causing blockage. High pressures may result in fracturing or daylighting. Biofouling or scaling may block injection lines or well screens. A lower permeability than expected may require change in design, as it will result in a smaller than anticipated ROI.
	Injection pressures are lower than expected.	This may indicate leaks in lines, or malfunctioning gauges. A higher permeability than expected may require change in design.
	Injection pressures suddenly drop and flow rate increases.	A preferential pathway (Section 3.6.1), fracture, or utility corridor may have been intercepted or an injection pressure fracture may have been created.
Physical Parameters	Conductivity, temperature, turbidity, or other indicator parameter of amendment (e.g., TOC or color) is observed at a nearby monitoring well (e.g., 3 m) at a lower than planned injection volume.	This type of result may indicate a connection or preferential pathway between wells. It may also indicate a higher K area of the site, resulting in a larger than anticipated fractured flow.
	Vapors, an unusual odor, or a change in color is observed at a monitoring well.	Unexpected reactions may be occurring either in the formation or with an adjacent sewer line. Injection into nonaqueous phase liquids (NAPL) may have occurred.
	Changes in conductivity, temperature, turbidity, or other indicator parameter of amendment (e.g., TOC or color) is not observed at an expected monitoring well, or is observed only at low levels.	Preferential pathways (Section 3.6.1) may be present, or an insufficient volume of fluid has been added to achieve the target distribution. Re-evaluate the expected injected volume to distribution relationship calculations and confirm that suitable volumes were added.
	Conductivity, temperature, turbidity, or other indicator parameter of amendment (e.g., TOC or color) is observed at a deeper interval than the injection interval.	Consider density-driven flow or preferential pathways (Section 3.6.1) that may be hindering the achievement of contact between amendment and targeted treatment interval.

Data Type	Scenario	Potential Implication
Observations in Soil or Bedrock Cores	Presence or lack of presence of amendment in offset cores.	Injected slurries or proppants typically may have a smaller ROI in coarse-grained formations and larger ROI in fine-grained formations as a result of soil fracturing. Revise injection volume based on effective porosity of the formation. Jetting may be required in coarse-grained soils. Cores are only a small area of the total ROI, so this could be just a sampling issue. Otherwise re-evaluate overall delivery approach or use other less targeted technologies to assess distribution or just rely on monitoring well impacts.

4.4.2 Performance Monitoring

▼*Read more*

Once the appropriate amendment and delivery technique for a site's unique conditions have been optimized, a performance monitoring strategy must be developed to assess performance and regulatory compliance during application, remedy operation, and post operation periods. This section describes performance and compliance monitoring configurations, decision parameters, optimization alternatives, contingency planning, and remedy transition planning. Performance monitoring includes techniques to assess field application of amendments, post application performance, and the overall long-term effects of the remedy. Note that both short-term and long-term performance monitoring should be reviewed to evaluate seasonal patterns, temporal changes, back-diffusion, and evidence that the site may not have been adequately characterized.

This section also presents optimization techniques that can be implemented during subsequent application events. Furthermore, this section includes a discussion of when remediation should be transitioned, whether to an alternative technology, MNA, or closure. Information in this section supports development of a site-specific plan; therefore, not all optimization activities are applicable to every site.

The intent of performance monitoring is to evaluate remedial progress upon successful injection and distribution of amendments. Performance monitoring compares conditions before, during, and after treatment using various performance indicators and metrics to determine a site's status. Some possibilities include:

- Progress toward remedial performance objectives (ITRC 2011c) is acceptable and objectives are being met.
- Total contaminant mass has been destroyed (see Section 4.4.5.2).
- Remedy optimization can meet objectives with greater efficiency.
- Performance is unacceptable and the remedy and supporting data must be re-evaluated.

A performance indicator should be defined in terms of the technology being used, targeted media, receptor location, and expected response of the subsurface to treatment by the technology. Typically and historically, a performance indicator is the contaminant concentration. However, other performance indicators may provide information regarding the mechanisms responsible for decreases in contaminant concentration such as mass flux to demonstrate source control, NAPL depletion rate, biodegradation rate, chemical oxidation/reduction rate.

Development of an effective performance monitoring strategy requires consideration of different factors, including:

- overall site remediation goals and objectives (ITRC 2011c) (e.g. plume containment, plume stability, mass flux reduction, mass decrease, attaining maximum contaminant limits (MCLs), or other performance standards)
- translation of overall remediation goals into remedial system

Performance objectives: ▼*Read more*

Performance objectives include specific measures used to determine whether or not the remedial action is successful in achieving site-related remedial goals or interim remedial milestones. Remedial performance objectives typically are site- and technology-specific, and based on the site-related remedial goals. They also vary depending on the type of contaminant being remediated (e.g. chlorinated volatile organics, petroleum hydrocarbons, metals, PCBs). When developing remedial system performance objectives, the practitioner should consider how the data will be used to evaluate progress, guide optimization, and demonstrate achievement of site remedial goals.

Performance indicators: ▼*Read more*

A performance indicator is a measurable or calculable feature of a remedial system or process that provides direct interpretive value to (1) remedial mechanisms or processes or (2) achievement of a remedial objective. A performance indicator should be defined in terms of the technology being used, targeted media, receptor location, and expected response of the subsurface to treatment by the technology. Typically and historically, a performance indicator is the contaminant concentration. However, other performance indicators may provide information regarding the mechanisms responsible for decreases in contaminant concentration (for example, percent of groundwater plume capture to demonstrate plume containment, mass flux to demonstrate source control, NAPL depletion rate, biodegradation rate).

Performance metrics: ▼*Read more*

A metric is a unit of measure; therefore, a performance metric is the unit of measure for a performance indicator.

Performance models: ▼*Read more*

A performance model is a predictive model that describes the expected course of the remediation process. It describes graphically and/or numerically how conditions are expected to change over time, as measured using appropriate performance indicators, from the current state until the performance objective is achieved. At many sites and for many remedial systems, no single performance model, indicator, and metric is likely to be adequate for assessing remedial performance; thus, conjunctive use of multiple metrics may be needed to evaluate performance.

The performance monitoring strategy should be directly related to the following factors.

- Site and TTZ characteristics, remedial design characterization, and associated CSM, at a resolution and scale(s) applicable to the treatment technology.
- expected behavior of the treatment system under optimal conditions
- common or reasonably anticipated shortcomings in treatment system operation
- common or reasonably anticipated shortcomings in treatment effectiveness
- expected time frame for attaining performance objectives
- compliance objectives

Often, it is useful to implement a data quality objectives (DQO) process to develop and document the technical rationale for a performance monitoring strategy (USEPA 2006a).

Because remedies at many groundwater contamination sites require a long time to achieve completion, performance indicators and metrics specific to interim remedies and goals can be helpful in evaluating progress toward ultimate site closure. Performance indicators and metrics should address:

- remedy operation (e.g. injection rate, ROI, beginning COC concentrations, concentration trends, amendment application rate) (see Section 4.4.1)
- remedy progress (e.g. rates of reduction of contaminant volume and/or mass, COC trends, microbial populations)
- remedial goal attainment (e.g. individual well COC concentration mean and confidence levels, individual well COC trends, overall COC trends, or alternatively, remediation goals based on contaminant flux and/or mass reduction rather than concentration-based goals)
- compliance with specified regulatory metrics

Identification of multiple performance indicators and metrics, consistent with technical approaches based on multiple lines of evidence, typically strengthens the data and information used to support decision-making throughout the remedy implementation process.

4.4.2.1 Monitoring Well Network

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Monitoring points used to monitor the performance of an in situ remedial action in meeting final remedial goals should ideally be located outside the designed area of influence for those injection units and be positioned to assess whether the remedial action is addressing the entire targeted contaminant plume. Several conditions can affect the representativeness of groundwater collected from injection wells and lead to uncertainty or overestimation of remedy performance:

- Data collected from injection wells, which are by definition located within the ROI could be misleading and exaggerate treatment performance.
- Amendments will likely accumulate in or near the injection well.
- Injection wells are susceptible to scaling and biofouling (see Section 3.6.1.2), depending on the natural geochemistry and amendments injected.
- Displacement of representative contaminated groundwater from the screened interval can occur due to injection of large volumes of amendment.
- Anisotropic distribution of amendments can occur due to heterogeneous geology or uncontrolled hydraulic fracturing.
- Thermal reactions within the ROI of the injectate may cause volatilization of some contaminants and may mobilize others.

It is useful to categorize the monitoring strategy individually within portions of the site or the TTZ. The monitoring strategy can be tailored specifically to the regulatory, operations, and optimization needs of each category. Examples of useful ways to subdivide a site or TTZ may include:

- background area
- source area
- NAPL zone
- contaminant plume
- plume fringe areas
- amendment TTZ
- contaminant reaction/treatment area
- geochemical transition zones
- compliance boundary

Background wells, source area monitoring wells, plume area and plume fringe monitoring wells, sentinel wells, and compliance boundary wells are typically included in the performance monitoring network (Figure 4-1) (2011c).

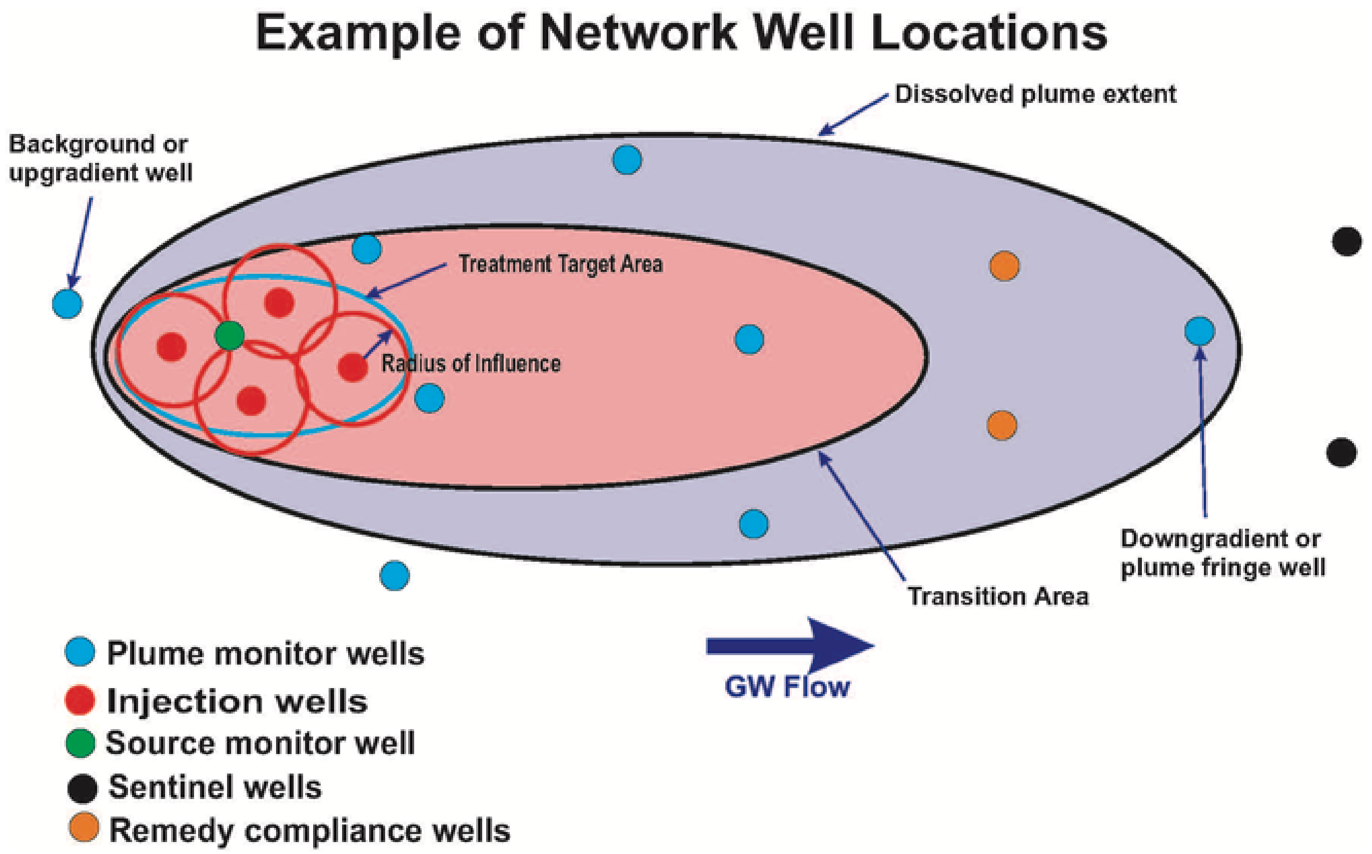

Figure 4-1. Example of network well locations

Within the treatment area monitoring wells should be used to assess performance. If the design assumes source reduction that will minimize flux leaving the source then additional monitoring wells would be outside the treatment area. The distance of monitoring wells from the injection wells will be dependent on site geology and the volume, rate, and pressure of amendments being injected. The number and spacing of monitoring locations should be a direct reflection of the complexity and heterogeneity of the TTZ. In complex hydrogeologic settings, performance monitoring may require wells in transects that are perpendicular to groundwater flow direction to monitor lateral components of the plume and to evaluate mass discharge. Intermediate and/or deep wells may be necessary to evaluate the vertical extent of the plume.

The monitoring program and network should also provide data that characterize changes within the geochemical transition zones. Changes in groundwater geochemistry within the treatment zone are an intended and necessary component of in situ treatment and are important performance indicators. These changes and associated secondary water quality effects may also extend beyond the treatment area and persist longer than the treatment time frame before typically returning to pretreatment conditions. Monitoring of geochemical transition zones may be important in an area beyond (i.e. downgradient of) the treatment zone and persist over a different time frame than monitoring focused on contaminant treatment.

Other questions to consider in developing a performance monitoring strategy include:

- Is the spatial distribution of monitoring points sufficient to map?
- Are the actual biogeochemical zones associated with treatment?
- What are the hydrodynamics within the treated area?
- Are there changes in treatment process parameters along flow paths?
- Are the monitoring wells inadvertently creating a preferential pathway for amendments?
- Are new performance monitoring wells needed to evaluate groundwater quality?
- What is the variability within the treatment area?
- Is the chemical analyte list sufficient to monitor and optimize?
- What is the actual treatment process?
- What is the metric for assessing remedy effectiveness?
- Are there secondary geochemical and water quality effects?
- Is sampling frequency and duration sufficient to:
    - ensure that the longevity and effectiveness of the amendments are taken into consideration?

  - optimize treatment operation after start-up?
  - monitor treatment process and performance in response to seasonal/annual change (for example, hydrodynamics, plume dynamics, treatment substrate availability)?
  - provide information in a timely manner to allow modifications and prevent noncompliance?

Performance monitoring is a critical step in assessing the efficacy of an in situ remedy, encompassing both data collection during (process monitoring) and after remedy implementation (remedial effectiveness monitoring). The subsections that follow discuss the elements of an appropriate monitoring program from baseline through compliance monitoring and focus on the evaluation of data to optimize performance of in situ remedies.

4.4.2.2 Monitoring Schedule

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Monitoring frequency may vary throughout the long-term monitoring program. It is common to initially begin with a relatively frequent monitoring schedule, which may then be modified, as site conditions are better understood. Projects with regular performance monitoring and evaluation of the results have a greater chance of achieving the remedial goals within desired time frames and potentially at a lower cost (USEPA 2017b).

The frequency of monitoring is dependent upon the type of amendment injected, anticipated rate of reaction, the groundwater flow velocity, distance to potential receptors, and the rate of change of key analytes (for example, primary contaminants and daughter products/intermediates). Longevity and effectiveness of the amendments play an important role in selecting initial to long-term sampling frequencies. For treatment technologies with fast kinetics (for example, abiotic-based treatment projects) the initial sampling frequency may start out hourly or daily until process monitoring parameters are stable (see Section 4.4.1) and then transition to quarterly, semiannual, or annual sampling. For treatment technologies with slower kinetics (enhanced bioremediation), process monitoring parameters may be measured weekly while microbial consortia and COCs and final degradation products may be sampled quarterly, semiannually, or annually. If the groundwater velocity is relatively fast, frequent sampling may be necessary to evaluate the treatment system such that optimization is initiated in a timely manner. Conversely, in aquifers where the velocity is slow, sampling more than semi-annually may be a waste of resources and provide unchanging data of limited value. Important information can be missed if the initial sampling is not executed soon after, or frequently enough following, implementation. However, it is very likely that once certain interim criteria are met, monitoring can be transitioned into a more cost-effective, less frequent (and in many cases fewer parameters) long-term plan (NAVFAC 2018).

The monitoring frequency should be sufficient to identify (as quickly as possible) when the implemented remedy is not performing as expected and requires potential modification (for example, reinjection of amendment(s), bioaugmentation, pH adjustment). Monitoring frequency and duration should illustrate that back-diffusion from matrix storage will not jeopardize long-term remedial objectives.

As a cost-savings and time-savings measure, analytical parameters that are inexpensive and quickly obtained are typically monitored more frequently during early performance monitoring. More complex analyses are recommended for long-term performance monitoring. For instance, establishment of microbial populations necessary to support bioremediation occurs more slowly than ISCO reactions, and therefore microbial analyses are not conducted immediately or with great frequency. However, it is necessary to assess whether ideal conditions to support microbial activity are being established. These water quality conditions are typically evaluated through low-cost analyses such as DO, ORP, and TOC on a frequent basis. Once the ideal water quality conditions are established, then it would be appropriate to evaluate changes to microbial community populations.

4.4.2.3 Baseline Monitoring

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Developing an effective baseline monitoring plan to evaluate progress toward achieving remedial objectives is a critical element of an in situ remedial action (ITRC 2005, 2011c; NJDEP 2017). Baseline conditions should be established prior to the initiation of remediation either by using historical soil or groundwater quality data and/or by conducting one or more separate baseline sampling events. Ideally, historical data should provide seasonal and temporal trends. Baseline data should be collected within 6 months of the design phase, particularly if site conditions are changing rapidly due to high groundwater velocity, extreme weather events (for example, recent hurricanes, flooding, drought), or activities that might impact site conditions (for example, new industrial or municipal water supply well, excavation, or heavy construction). If a post-remedial design baseline sampling event is performed, it should be conducted to allow sufficient time for the results to be evaluated prior to the initiation of remediation. Baseline monitoring also establishes pretreatment conditions for comparison with data collected during and following in situ treatment to assess the effectiveness and protectiveness of in situ remedial technologies.

Baseline analytical parameters will differ depending on the COCs targeted and the amendment(s) selected for in situ remediation. Section 4.4.4 list the general parameters to be analyzed during baseline monitoring and the subsequent stages of early and long-term performance monitoring and compliance monitoring. Use professional judgement to determine the frequency of sampling each parameter as appropriate for the amendment selected, as the analyses mentioned are not exclusive or exhaustive. The vendor providing the amendment is also a good resource for establishing a sampling and analysis plan.

Establishing baseline conditions includes the analysis of soil and groundwater samples from the site for target contaminant(s), potential biological or abiotic degradation byproducts, general geochemistry, co-contaminants that may not be affected by the selected amendment or that may interfere with the in situ remediation process, and naturally occurring constituents or geochemistry that may interfere with the in situ remediation process. This may include high resolution profiling techniques. It may also include parameters that are naturally occurring and unique to the amendment such as sodium or potassium. Although baseline monitoring of soil conditions is an important criterion for many remediation sites, performance monitoring is generally performed through the evaluation of groundwater data because it is less costly to collect and more homogeneous than soil. The baseline sampling event should be conducted at the same locations as the proposed remediation monitoring locations, which should include an upgradient background, plume source, midplume, plume fringe, and sentinel wells as illustrated in Section 4.4.2.1. If background contamination is present on-site from off-site sources, additional sampling of background monitoring wells may be warranted.

Groundwater sampling parameters should include the chemical constituents in the amendment to be injected (for example, for compatibility testing) and any constituents that may cause groundwater quality to exceed a numeric groundwater or surface water criterion (for example, sulfate in a sodium persulfate application). Comparison of baseline and post-treatment sampling results may indicate the criteria were exceeded due to natural conditions, or pretreatment conditions. Natural or background conditions could potentially be determined from nearby, unaffected or upgradient wells if insufficient preinjection data are available.

In certain cases, the monitoring plan should include sampling of other media as necessary to address risks to all potentially affected media (for example, surface water, groundwater, soil, soil vapor, indoor air). Planning should consider possible physical displacement of any subsurface contaminants by the amendment injections (in any phase or media), as well as technology-specific impacts (for example, the physical displacement of light non-aqueous phase liquid (LNAPL) or vapors, which may subsequently cause or exacerbate vapor intrusion into a nearby building) or transfer of contaminants and amendments from one medium to another.

4.4.2.4 Compliance Monitoring

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Compliance monitoring is performed to assess whether the remedy has been successful in meeting the interim or final regulatory goals established and if other compliance metrics are being met. An example of a compliance metric is an allowed increase in TDS of 20% above background, but not exceeding the water quality standard for TDS. Compliance monitoring is typically performed at the edge of the plume; immediately upgradient of a stream or other protected resource; at the property line; or for certain Resource Conservation and Recovery Act (RCRA) and non-RCRA landfills, impoundments and similar projects, at the point of compliance for a regulated unit. Injection wells are subject to a variety of issues that limit their usefulness in performance monitoring and prohibit their use for compliance monitoring in all but the most extenuating circumstances.

Referring back to Section 4.4.2.1 compliance monitoring wells are likely to be sentinel wells, plume fringe wells, or downgradient plume monitoring wells, depending on the interim compliance standard the remedy is expected to achieve. The parameters monitored at the compliance point include, at a minimum, field parameters (for example, pH, specific conductance, temperature, turbidity, DO, and ORP), site-specific COCs, and any indicator parameters applicable to the amendments injected. For instance, an increase in dissolved arsenic concentration is a common side effect of anaerobic bioremediation. It is important to monitor arsenic to determine if remediation efforts have mobilized and threaten water quality at the point of compliance, property line, or other predetermined compliance monitoring point. Other examples are provided in Tables 2-3 and 4-2 through 4-6.

Depending on the (see Section 5) where the project is located, there may be additional monitoring requirements for compliance purposes. Most states require permits for the injection of amendments into the subsurface, typically called UIC permits. These permits may have various compliance metrics that must be met. The UIC permit may require additional monitoring wells and specific compliance monitoring parameters.

As an example, in 2008 and updated in 2015, the California Central Valley Regional Water Quality Control Board (CCVRWQCB 2015) developed a general order (similar to a permit) for in situ cleanup projects. That order provides information requirements for the proponent to provide to be covered under the order. Some of the information required includes a proposed monitoring plan to assess the water quality impacts from the project, delineation of compliance points and transition points, and a contingency plan with trigger metrics for implementation. The order and accompanying *Notice of Applicability* include water quality objectives that must be met, groundwater quality limitations and specifications, and discharge prohibitions. The design, monitoring, and optimization of the project can be affected by complying with the order. There is also a working group at the Los Angeles RWQCB that issued technical guidance in 2008, “Subsurface injection of ISRR” (LARWQB 2008).

Another example exists in the Eastern Surplus Company Superfund Site, Southern Plume, Maine Department of Environmental Protection (USEPA 2018a). After discovering contaminated groundwater in two separate plumes (northern and southern plumes), remedial actions for a combined groundwater pump and treat and ISCO were begun at both plumes. VOC contaminant concentrations within the southern plume have decreased to below concentration goals, which are based on U.S. Environmental Protection Agency (USEPA) maximum contaminant levels (MCL) or Maine’s maximum exposure guidelines (MEG), whichever is lower for the COC. USEPA performed a bench-scale study in 2011 and a pilot study in 2012–2013 of EISB in the northern plume. Based on the positive impact, USEPA is preparing to expand to a full-scale implementation of EISB.

Thus, a project proponent needs to obtain the specific requirements for the state where the project is located. These requirements may have profound impacts on the design and optimization of the in situ remedy project.

4.4.3 General Parameters

Parameter selection depends on the type of in situ technologies applied. Some general baseline parameters common to various in situ methods are evaluated to measure the effect of in situ remediation relative to remedial objectives, compliance criteria, or operational end points. These parameters may be collected in any and/or all media:

- NAPL— ▼*Read more*
- Vapor— ▼*Read more*

Sampling parameters, timing, and frequency should be selected based on how long the injected amendments are expected to be active and effective. Due to the relatively lower cost and ease of collecting groundwater samples, it is common to collect groundwater samples more frequently during a remedial program. Therefore, most of the discussion in this section focuses on groundwater monitoring. However, professional judgement should be used to determine when, where, and how frequently other media should be sampled and how to evaluate that data.

The geochemical, hydrogeologic, and microbial data should be used to characterize both pre-implementation chemical conditions and hydrogeologic conditions (see Section 2.2). Evaluation of chemical, physical, or biological processes in the subsurface that affect remedy performance and the distribution of COCs depends on the media monitored and potential exposure pathways. Subsurface media may include NAPL, aquifer matrix materials, soil gas, groundwater, seeps, and surface water. If feasible, the preinjection degradation rates should be compared to postinjection rates to measure the effectiveness of in situ technology relative to natural attenuation. Some suggested baseline monitoring parameters that may be applicable are listed below and should serve as a starting point for a site-specific parameter list. Based on site-specific conditions and remedial objectives, additional parameters may be warranted as discussed in Section 2.3 and Section 4.4.4. Further information may also be found in the Appendix A fact sheets for various amendments.

Groundwater Elevations: ▼*Read more*

Groundwater elevations should be monitored to evaluate the hydraulic connection between the injection well locations and monitoring wells. Hydraulic gradient information should be calculated to estimate the most probable contaminant migration direction and velocity. For larger treatment zones or more complex hydrogeology (for example, interactions between the unconsolidated and bedrock aquifers, tidal or seasonal fluctuations in groundwater, karst, etc.), transducers with data loggers would provide additional information and better capture variability over time. If differences in static water levels during process monitoring are not consistent with expectations, or if a shift in hydraulic gradient or preferential pathways is noted, then additional assessment may be warranted.

Tracers: ▼*Read more*

Groundwater flow direction and preferential pathways that influence the distribution of target contaminants and injected amendments may not be apparent from groundwater elevations and gradients. It can be useful to evaluate site hydrogeology using tracers such as dyes, temperature-controlled water, deionized water, deuterium -which may require special permits, ionic salts, or stable isotopes specifically emplaced with amendments or by using the parent amendments (e.g. TOC, DO, sulfates) or reaction byproducts such as methane. Compounds that degrade, transform, or partition out of the dissolved phase may or may not be useful qualitatively as tracers. Tracer data may be used for quantitative evaluation of distribution, velocity, and remediation time frame (Shook 2004).

Field and Water Quality Parameter Measurement: ▼*Read more*

Common field parameters include pH, DO, ORP, temperature, turbidity, and specific conductance (see Section 2.2). Most in situ injection strategies will alter these parameters by design. Establishing a baseline and then monitoring over time following amendment injection(s) will inform the effectiveness and duration of treatment. For larger treatment zones or more complex hydrogeology (for example, interactions between the unconsolidated and bedrock aquifers), data loggers would provide additional information and better capture variability over time. Data loggers that measure temperature or specific conductivity as well as pressure may be useful. Field measurement of ferrous iron may also be appropriate for some sites, particularly those involving anaerobic bioremediation.

General Geochemistry: ▼*Read more*

Parameters may include nitrate and nitrite nitrogen, ammonia, total and dissolved iron, total and dissolved manganese, sulfate, sulfide, chloride, sodium, potassium, calcium, magnesium, fluoride, hardness (as $CaCO_3$), alkalinity, dissolved carbon dioxide, dissolved methane, TDS, dissolved organic carbon (DOC), TOC, chemical oxidant demand (COD), and biological oxidant demand (BOD). These parameters are important to understanding the natural attenuation mechanisms underway in advance of treatment and the potential success or barriers to success for specific treatment amendments. If relevant, confirm that nutrients (nitrogen and phosphorus) required for the microbial metabolism are present in adequate amounts.

Metals Concentrations: ▼*Read more*

Total and dissolved metals concentrations such as lead, chromium, arsenic, cadmium, zinc in groundwater should be monitored as needed and relevant to specific treatment technologies, as some in situ technologies may promote temporary mobilization of metals within the treatment zone. Generally, metals mobilization declines with time and distance from the treatment zone as geochemical conditions normalize. Therefore, monitoring outside the treatment zone may confirm metals mobilization is restricted to a limited area. The initial investigation of soil and groundwater (that is, during development of the CSM) should include analysis for arsenic, barium, cadmium, chromium (including hexavalent chromium), copper, iron, lead, manganese, nickel, selenium, and if relevant, beryllium and antimony. The appropriate list of metals and analytes would depend on site conditions and amendments used. Typically, the practitioner will be evaluating the reduction or oxidation of metals. Note that upon completion of the remedial action, it may take several months to years for metals concentration to return to background concentrations. The remedial action plan and decision documents should be written to account for the dissolved metals to persist at concentrations exceeding the goal for a period of time. In cases where the COC is a metal, rebound testing will need to be conducted for several years to verify the remedy was successful at immobilizing metals.

Specific Amendments and Parameters: ▼*Read more*

Each amendment used to treat soil and groundwater requires delivery and maintenance of those amendments to the targeted treatment area. Concentrations of the parent amendment and/or compounds or other indicators associated with the selected amendment (e.g. TOC, DO) should be monitored to confirm delivery and distribution and to track consumption to evaluate injection frequency, dosage, and quantity.

Contaminants of Concern Analysis: ▼*Read more*

COCs should be analyzed to measure the degree and extent of treatment in the target area, evaluate rebound following treatment events, evaluate the effectiveness of the treatment at the plume fringe, and optimize the delivery and dosage for future injections. For example, estimates of the baseline total contaminant mass in the subsurface can be used for comparison during process (see section 4.4.1) and performance monitoring (see Section 4.4.2) to assess the overall effectiveness of the remedial approach for the site. The baseline target contaminant concentrations are also used for comparison with concentrations remaining in soil and/or groundwater.

Contaminant Breakdown and End Products: ▼*Read more*

Intermediary compounds formed during treatment reactions (see Section 2.2) are important indicators of progress and should be monitored throughout implementation to understand treatment effectiveness. In some cases, the only product of remediation will be the end product of the treatment reactions. Measurement of the intermediary and end products of remediation is important to confirm that amendments are not masking or displacing the target compounds and that transformation and destruction are occurring rather than migration and repartitioning. It is also important to evaluate whether or not breakdown products are accumulating, which in biological remedies is an indicator that the process is stalling, possibly because the appropriate genes are not expressed for complete degradation or something is inhibiting complete degradation, and in chemical oxidation remedies is an indicator of unwanted byproducts that require further remediation or of incomplete oxidation of intermediary products. Furthermore, it is important to understand the toxicity, fate, and transport of daughter products and intermediates, as some byproducts are more mobile than the parent compounds.

Compound-Specific Isotopic Analysis (CSIA): ▼*Read more*

In some cases where dissolved phase analysis of target compounds, breakdown products, and end products do not demonstrate the expected level of degradation, isotopic analysis may be helpful in evaluating treatment performance. If repartitioning of target compounds is a driver of dissolved phase concentrations and intermediary byproducts are not available, shifts in isotopic signature within the target compounds, compared to baseline results, may demonstrate selective and more rapid treatment of molecules containing lighter isotopes. (see Section 2.2)

Microbial Analysis: ▼*Read more*

(see Section 2.2) In cases where pre-implementation or pilot-scale degradation of target compounds is not evident such that biological processes can be inferred from the presence of intermediary or end products, analysis of the biological community and confirmation of the necessary microorganisms may be required. Microbial analysis can be helpful in the baseline monitoring to confirm feasibility of an approach and to confirm the persistent support of microbial communities through treatment and long-term performance monitoring.

4.4.4 Technology-Specific Parameters

The following tables describe some of the analytical parameters that may be used to monitor the performance of various remedies. Although not meant to be prescriptive or exhaustive, the information in the tables can be used to develop a site-specific monitoring plan. For certain amendments, such as activated carbon-based injectates, the general parameters described in Section 4.4.3 are sufficient. Additional information is available in the amendment-specific fact sheets in Appendix A. The general categories include:

- anaerobic biostimulation (Table 4-2 and A1.2, A1.3, A1.4, A3.1, A3.2, A3.3)
- aerobic biostimulation (Table 4-3 and A1.1, A1.2, A1.4, A3.1, A3.2, A3.3)
- chemical oxidation (Table 4-4 and A2.1, A3.2)
- chemical reduction (Table 4-5, A2.2, A2.3, A3.2)
- surfactant and co-solvent flushing (Table 4-6, A2.5)

Table 4-2. Analytical parameters for anaerobic biostimulation (with or without bioaugmentation).

Parameter	Interpretation Guidelines	Recommendations
Contaminant concentrations	Progress is denoted by a reduction of parent COC concentrations and an increase in degradation products; build-up of degradation products could signal stalling.	If parent concentrations are declining but degradation products are not produced, there may be an alternate pathway (e.g., abiotic instead of reductive dechlorination).
Contaminant breakdown products	Breakdown products should be short-lived and reduce with time if the degradation is continuing to the desired end products. Changes in total molar concentrations of the parent and breakdown products should be assessed to verify full degradation.	If undesirable breakdown products continue to increase, then adjustments may be needed to stimulate greater transformation toward the desired end products.
Ultimate end products (e.g., methane, ethene, ethane, chloride, propene)	Presence confirms degradation of chlorinated solvents or conditions suitable for sulfate reduction and methanogenesis.	If sulfate reduction and methane are not observed and ORP is greater than approximately –120 mV, conditions do not exist for sulfate reduction and methanogenesis that support dechlorination.
Field parameters—pH	Microbes typically require neutral pH (optimal range is 6.8–7.5; generally required range is 6.0–8.5).	Select microbial consortia that are suited for low pH environments. Amend with sodium bicarbonate, sodium carbonate, or other additives to adjust pH; verify distribution if amendment is unsuccessful.
Field parameters—DO and ORP	DO should be <0.5 mg/l and ORP should be negative; if DO and ORP values are conflicting, the treatment zone may not be properly buffered or gases formed by injected materials may be causing instruments to read incorrectly.	If high DO or high ORP is observed in pockets, anisotropy may be hindering distribution by lowering the ROI in certain areas. Evaluate injection spacing in these areas to improve coverage. Under neutral pH, denitrification occurs when ORP values are between +50 and –50 mV; sulfate-reducing between –50 and –250 mV, and methanogenesis occurs at –200 to –400 mV.
Field parameters (e.g., temperature, specific conductance)	An increase in temperature or specific conductance may indicate injection reagents transport and could be used to evaluate ROI.	Each species of bacteria has an optimal range of temperature for growth. Verify that selected consortia meet site characteristics during the selection process because aquifer temperature cannot be changed.
Water level and NAPL thickness	Mounding or increased hydraulic gradients can be induced during injection events. NAPL can also be mobilized.	Determine groundwater flow direction and the hydraulic connection between injection wells and monitoring wells.
TOC	TOC includes both naturally occurring organic carbon (such as humus) and organic carbon contamination, e.g., benzene. TOC values above approximately 50 mg/L indicate carbon levels that, if biologically available, could foster cometabolism.	Over time TOC will decline again to pre-remediation levels. This, combined with aquifer flow and transport information, can indicate when the substrate is depleted.

Parameter	**Interpretation Guidelines**	**Recommendations**
Tracers (e.g., bromide, potassium, TOC)	If carbon or nutrients are injected, they can be used as a tracer to evaluate ROI and calculate travel times. TOC is an indicator of donor longevity, and trend analysis should predict when secondary injection is necessary.	If tracers are not observed where anticipated, review best practices for emplacement techniques. The sorption of carbon amendments to aquifer material complicates delivery.
Ferrous (Fe^{+2}) and ferric (Fe^{+3}) iron and other site-specific metals	The ratio of ferrous (Fe^{+2}) to ferric (Fe^{+3}) provides information on how reducing the groundwater is, the potential for abiotic reductive dechlorination via ferrous iron, and the presence of iron as electron acceptors for biological activity.	Under reducing conditions, ferric iron will pick up an electron to become ferrous iron. If the observed ratio is not as expected, this is an indication that ideal conditions have not been established. Ferrous iron values >1 mg/L are indicative of iron reduction in the absence of nitrate.
Reduced or mobilized metals (Mn^{-2}, Cr^{+6}, As^{+3})	Various metals may be naturally present in groundwater based on provenance and mineralogy.	These should be assessed on a site-specific basis as part of in situ remediation planning.
Alkalinity	Alkalinity should be >20 mg/L or fermentation may cause further decline in pH.	Select a buffering agent such as calcium carbonate that improves the alkalinity. Alkalinity needs to be sufficient to allow proper buffering so pH does not drop as a result of acids generated during the fermentation process.
Sulfate/sulfite/sulfide	Sulfate concentration <20 mg/l is indicative of sulfate-reducing conditions.	Amendment dosing should be designed to reduce high sulfate when present. If hydrogen sulfide is formed, this can be toxic to microbes.
Nitrate/nitrite	Nitrate is the first choice for electron acceptor after oxygen is depleted and generates a sequence of byproducts consisting of nitrite ions and gases (nitric oxide, nitrous oxide, and nitrogen).	Amendment dosing should be designed to reduce high nitrate when present; nitrite may be observed when nitrate is reduced. Nitrate concentrations <1 mg/L are indicative of denitrification.
Volatile fatty acids (VFAs) (e.g., lactic acid, acetic acid, pyruvic acid, propionic acid, butyric acid)	Presence confirms the fermentation of carbon substrates such as EVO and lecithin.	If VFAs are not present in an area with high TOC, then fermentation is not occurring. Determine if pH, DO, and ORP need to be adjusted to promote biological activity. If VFAs are present, assess whether the proper microbial consortia are present. Amend if necessary.
Vapor measurements (e.g., PID, USEPA Method TO-15, LEL)	High levels of gases are an indicator of both successful bioremediation and potential health and safety or vapor intrusion concerns.	Evaluate risk of vapor intrusion and/or dangerous gas levels. Mitigate if necessary. Reduce frequency of injections to control methane. Verify pH has not dropped.

Parameter	**Interpretation Guidelines**	**Recommendations**
Microbial analysis—gene-specific Section 4.4.3 and 4.4.4.1)	Microbial analysis evaluates a wide range of anaerobic and aerobic degraders. *Dehalococcoides mccartyi* (DHC) and DHC-related strains are known to degrade chlorinated ethenes; DHB (*Dehalobacter*) strains are known to degrade chlorinated ethanes and methanes; DHG (*Dehalogenimonas*) strains are known to degrade chlorinated propanes and chlorinated ethenes; vinyl chloride reductase gene is known to convert VC to ethene (commonly referred to as vinyl chloride reductase (VCR) and BAV genes).	Evaluate if useful microbes are present or if competing microbes are hindering remediation. Microbial analysis provides quantification of important organisms and functional genes responsible for biodegradation of a group of contaminants and therefore more comprehensive site assessment (ITRC 2011b, c).
	Use when degradation of parent COCs and/or daughter products is not discernable and is required.	Verify anaerobic microbial populations are present; if not, consider amending.

Table 4-3. Analytical parameters for aerobic biostimulation (with or without bioaugmentation)

Parameter	**Interpretation Guidelines**	**Recommendations**
Contaminant concentrations	Progress is denoted by a reduction of parent COC concentrations; byproducts detection may be difficult. Seasonal or water table fluctuations should be taken into consideration.	If parent concentrations are declining but degradation products are not produced, may be an alternate pathway. Look for ultimate end products or CSIA data to prove degradation.
Contaminant breakdown products	Breakdown products should be short-lived and reduce with time if the degradation is continuing to the desired end products.	If undesirable breakdown products continue to increase, then adjustments may be needed to stimulate greater transformation toward the desired end products.
Ultimate end products (e.g., oxygen and CO_2 gases, dissolved CO_2)	Presence confirms aerobic degradation to end products.	These end products may quickly dissipate in the vadose zone.
Field parameters (e.g., pH, temperature, specific conductance, DO, ORP)	Microbes typically require neutral pH (ideal range is 6.0–8).	Adjust pH if necessary.
Field parameters—DO and ORP	DO should be >2 mg/l and ORP should be positive.	If DO or ORP is outside the recommendation, improve oxygen distribution.
Water level and NAPL thickness	Mounding or increased hydraulic gradients can be induced during injection events. NAPL can also be mobilized.	Determine groundwater flow direction and the hydraulic connection between injection wells and monitoring wells.

Parameter	Interpretation Guidelines	Recommendations
Tracers (e.g., bromide, potassium, TOC)	If gas carbon or nutrients are injected, they can be used as a tracer to evaluate ROI and calculate travel times. Elevated nutrients can be an indicator of donor longevity and trend analysis should predict when additional injection is necessary.	Observe ROI and travel times.
Water quality parameters (e.g., sulfate/sulfite, nitrate/nitrite, alkalinity, propane, TDS)	High TDS can be inhibitory to microbial activity.	For aerobic cometabolic bioremediation of CVOCs and 1,4-dioxane, propane may be necessary.
Microbial analysis—gene-specific or QuantArray (Section 4.4.3 and 4.4.4.1)	QuantArray evaluates a wide range of aerobic and anaerobic degraders.	Evaluate if useful microbes are present or if competing microbes are hindering remediation.
CSIA (Section 4.3 and Section 4.4.4.2)	Use when degradation of parent COCs is not discernable and is required.	Verify aerobic microbial populations are present; if not, consider amending.

Table 4-4. Analytical parameters for chemical oxidation

Parameter	Interpretation guidelines	Recommendations
Contaminant concentrations	Progress is denoted by a reduction of parent COC concentrations.	If COC concentrations are unchanged, evaluate distribution and effectiveness of selected oxidant (e.g., permanganate will not oxidize ethanes).
Contaminant breakdown products	Breakdown products should be short-lived and reduce with time if the degradation is continuing to the desired end products.	If undesirable breakdown products continue to increase, then adjustments may be needed to stimulate greater transformation toward the desired end products.
Ultimate end products (e.g., acetone, carbon disulfide, carbon dioxide, chloride)	Presence confirms degradation.	These end products may quickly dissipate in the vadose zone.
Field parameters (e.g., pH, temperature, specific conductance, DO, ORP, pressure, ferrous iron, hydrocarbon gases, LEL, CO_2)	Certain reactions require low pH (ideal range is 4–6); amend if necessary. In the case of alkaline activation of some oxidants, pH should be confirmed to be above targets, typically in the range of greater than 10.5 and < 12.	Adjust pH as necessary. Temperature and conductivity are often elevated during ISCO application and can be used to evaluate ROI during process monitoring.
Water level and NAPL thickness	Mounding or increased hydraulic gradients can be induced during injection events. NAPL can also be mobilized.	Determine groundwater flow direction and the hydraulic connection between injection well locations and monitoring wells.
Metals (e.g., arsenic, chromium, lead, zinc, and other site-specific or amendment-specific metals)	Metals can leach from the geology/soil at concentrations that exceed regulatory standards.	Monitor secondary effects of ISCO application.

Parameter	Interpretation guidelines	Recommendations
Natural oxidant demand (NOD)	Determine the oxidant demand of the existing biogeochemistry and account for it when calculating the amount of amendment needed. A high NOD may preclude the selection of ISCO as cost-effective. COD, soil oxidant demand (SOD), and total oxidant demand (TOD) are related terms.	Evaluate oxidant demand required to overcome properties of the aquifer. This is typically a design parameter not used during performance monitoring. Multiple applications of a chemical oxidant may be required to overcome NOD such that COD can be adequately addressed.
TOC	TOC provides a general indication of the amount of oxidant that will be needed, if a soil sample cannot be collected for testing.	It is best to rely on NOD, COD, or TOD when using chemical oxidation amendments.
Amendment-specific parameters (e.g., manganese, sulfate, sodium, potassium, ozone), amendment components (H_2O_2, persulfate, permanganate, ozone)	Amendments can be used as a tracer to evaluate ROI and calculate travel times if the reaction with contaminants and soil minerals or organics is accounted for. May need to monitor for components of amendments if there are components that present a water quality concern.	Evaluate ROI and travel times.
Water quality parameters—TDS	TDS is a measure of the combined organic and inorganic substances in water, primarily minerals and salts.	Some states have compliance values for TDS and/or individual salts or minerals.
Sample representativeness	Oxidants such as permanganate and persulfate if present in the groundwater samples after collecting for analysis may continue to oxidize the contaminants slowly until analysis.	Although storing the sample at 4°C may inhibit the oxidation of contaminants, ascorbic acid or sodium ascorbate, as a preservative, is suggested to neutralize the residual oxidant (USEPA 2012b).

Table 4-5. Analytical parameters for chemical reduction

Parameter	Interpretation guidelines	Recommendations
Contaminant concentrations	Monitor change relative to baseline.	If COC concentrations have not been reduced, verify distribution of amendments.
Contaminant breakdown products	Breakdown products should be short-lived and reduce with time if the degradation is continuing to the desired end products.	If undesirable breakdown products continue to increase, then adjustments may be needed to stimulate greater transformation toward the desired end products.
Secondary water quality impacts (e.g., methyl ethyl ketone and acetone)	Concentrations typically attenuate rapidly to background concentrations (Fowler 2011).	Baseline concentrations of these contaminants should be established and included in performance monitoring to confirm this expected result.
Field parameters (e.g., pH, temperature, specific conductance, DO, ORP)	DO should be <1 mg/l and ORP should be negative; specific conductance should be not be affected by ISCR reagents until the iron is converted to ferric or ferrous forms. High specific conductance may suggest fouling.	Evaluate amendment distribution if DO and ORP are not reduced. Under neutral pH, denitrification occurs when ORP values are between +50 and –50 mV; sulfate-reducing between –50 and –250 mV, and methanogenesis occurs at –200 to –400 mV.

Parameter	**Interpretation guidelines**	**Recommendations**
Water level and NAPL thickness	Mounding or increased hydraulic gradients can be induced during injection events. NAPL can also be mobilized.	Determine groundwater flow direction and the hydraulic connection between injection wells and monitoring wells. Extreme mounding/injection pressures in injection wells may indicate scaling, fouling, or improper construction/development.
Water quality parameters—TDS	TDS is a measure of the combined organic and inorganic substances in water, primarily minerals and salts.	Some states have compliance values for TDS and/or individual salts or minerals.
Metals (e.g., iron, manganese, arsenic, and other site-specific or amendment-specific metals)	Reduction process can release dissolved concentrations of iron, manganese, and arsenic into the aquifer above water quality standards.	Minimize reduction conditions to the extent practicable while still allowing for desired processes for contaminant reduction.
CSIA (Section 4.3 and Section 4.4.4.2)	Degradation of COCs is not discernable and is required (e.g., areas with high concentrations near NAPL).	Use CSIA to discern low levels of degradation

Table 4-6. Analytical parameters for surfactant and co-solvent flushing

Parameter	**Interpretation guidelines**	**Recommendations**
Contaminant concentrations	Monitor change relative to baseline. Expect contaminant concentrations to rise at least an order of magnitude, if not more, during the flushing operation and within the flushing zone. If this does not happen then there is likely a problem with the flushing action.	If COC concentrations have not been reduced following the flushing action, verify distribution of amendments. If dissolved COC concentrations have increased in unexpected areas due to surfactant/co-solvent addition, assess need and options for containment/control or removal.
Amendment breakdown products	Some co-solvents and surfactants can transform or be biodegraded to other compounds (e.g., certain alcohols to acetone). Breakdown products should be short-lived and reduce with time, but in some cases may pose an exposure risk or treatment challenge. Appropriately specified shear-thinning fluids will rapidly biodegrade, often to low molecular weight organics and carbon dioxide. Limited dihydrogen and methane production is possible.	If undesirable breakdown products continue to increase, then adjustments may be needed to stimulate greater transformation toward the desired end products.

Parameter	Interpretation guidelines	Recommendations
NAPL thickness/distribution	The mobilization of NAPL by the amendments would be expected to reduce apparent product thickness in target areas. With effective design and implementation greater than 90–95% NAPL saturation reduction can be expected. If decreases are not observed, adjustments are necessary. Injection may displace NAPL to adjoining areas (laterally or vertically) and lead to increases in NAPL footprint or thickness. NAPL transmissivity can also be estimated, but the change in surface tension of the NAPL due to the amendments may change NAPL transmissivity substantially.	If expected reductions in NAPL thickness and distribution are not observed, reassess injection and recovery spacing, delivery method, or amendment dosage. If NAPL appears to be displaced, assess injection locations (e.g., work from outside inward), pressures, and volumes and consider steps to control or remove displaced NAPL.
Water levels	Monitor piezometric response to injection as a line of evidence for amendment delivery flow paths, and possible displacement of NAPL.	If piezometric responses are not observed as expected, evaluate hydrogeology and revise conceptual model; adjust injection and recovery locations, depths, and pressures. 0
NAPL mass/volume recovery	The amount of NAPL recovered indicates fundamental performance of surfactant or co-solvent flushing. NAPL recovery is difficult to accurately quantify due to the amendment/NAPL/water interaction and the likelihood of emulsions. Separation processes can allow better quantification.	The amount of product recovered (relative to baseline, if a recovery system was initially in place before the flushing) is assessed to determine if amendments are contacting the NAPL. Depth and location of injection and recovery are adjusted if recovery changes miss expected levels.
Concentration of amendments	Anionic and nonionic surfactant and co-solvent concentrations are monitored to assess the flow paths and adequacy of concentrations for optimally mobilizing NAPL through micelle formation.	Reassess location, depth, volume, and delivery pressure of amendment injections to establish adequate concentrations of surfactants and other components such as shear-thinning fluid polymer to mobilize NAPL.
Tracers (e.g., methylene blue active substances (MBAS), cobalt thiocyanate active substances (CTAS))	Because other subsurface constituents may react with the MBAS or CTAS, it is important to obtain a preinjection baseline analysis. MBAS mostly picks up anionic surfactants and CTAS mostly nonionic surfactants. Some surfactants cannot be detected by either method.	Reassess location, depth, volume, and delivery pressure of amendment injections to establish adequate concentrations of surfactants to mobilize NAPL.

There are many remediation sites where multiple remediation technologies have been or are being pilot tested, deployed sequentially, or deployed simultaneously (by design or otherwise) (Appendix E.10, LNAPL Remediation Combining Mobile Dual Phase Extraction with Concurrent Injection of a Carbon-based Amendment). Because the application of most remediation technology classes involves the temporary or permanent alteration of subsurface conditions, it is appropriate to evaluate the potential impacts the other technologies may have on the effectiveness of the proposed technology. For instance, significant organic carbon increase may exert a significant oxidant load above and beyond NOD. The types of analytical tests used for a site-specific monitoring program will vary depending on the chemicals known or suspected of being used previously (either the contaminant or amendment), the amendments expected to be used in the remedial action, and the local geology and geochemistry.

Molecular diagnostics such as quantifying the abundance of degradative bacteria (Section 4.4.4.1 and Section 4.4.4.2) are often included in the analytical suite to serve as additional lines of evidence to confirm contaminant degradation. Given their expense, however, these analyses are generally included less frequently (or applied at only a subset of wells within the network) than the monitoring of primary COCs and geochemistry. Additional information beyond what is provided below may be found in see “Environmental Molecular Diagnostics—Facts Sheets” (ITRC 2011b).

4.4.4.1 Abundance of Bacterial Groups

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Monitoring of target compounds and intermediary and end products during pilot- or full-scale implementation may be sufficient to confirm full degradation of target compounds. However, in some cases additional data regarding the microbial community are necessary to assess feasibility or understand and augment performance. Ongoing monitoring of targeted key organisms by quantitative polymerase chain reaction (qPCR) and the overall microbial community diversity by next generation sequencing (NGS) can measure the response of a site’s microbial community to remedial activities (ITRC 2011b) and (Shook 2004). These measurements can indicate whether the microbial community is sufficient to support ongoing biodegradation of the contaminant(s) or whether bioaugmentation or other amendments may be necessary. After enhanced bioremediation, and particularly after bioaugmentation, testing to confirm introduction, increase in abundance, and spread of key biodegradative organisms helps gauge the success of the remedy.

Microorganisms (bacteria) break down contaminants. Molecular tools including qPCR tests or NGS can be used to measure the presence and quantity of specific microorganisms that are capable of biodegradation of targeted contaminants. The use of molecular tools can address these questions:

- Are microorganisms present that are capable of degrading the contaminant(s)? If so, how many and where?
- Is MNA feasible?
- Are amendments required? If so, which nutrients and how much?
- Is bioaugmentation necessary?

Detection of specific microbial groups known to be capable of degrading a contaminant provides one line of evidence that bioremediation may be possible (ITRC 2011b, 2013a).

4.4.4.2 Shifts in Isotopic Signature

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For the most technically challenging projects, additional tools can be used to monitor and evaluate performance. In the course of many biochemical and abiotic reactions, molecules containing lighter isotopes (for example ^{12}C) tend to react more rapidly than molecules containing heavier isotopes (for example ^{13}C). As the reaction proceeds, the ratio of stable isotopes in the material that remains behind becomes isotopically heavier or enriched. This shift in the ratio of ^{12}C to ^{13}C can be measured by CSIA and can provide unequivocal evidence of degradation. It can also provide information for a direct calculation of degradation rates, thus providing data in support of two lines of evidence of contaminant degradation. For more information see ITRC’s “Environmental Molecular Diagnostics” technical and regulatory guidance document, chapter 3 (ITRC 2013a).

Each injection campaign is followed by a series of stages during which different processes dominate. Knowing what occurs in those stages is fundamental to knowing if an injection event was successful and if further injections are warranted. For example, following ISCO, the first stage is destruction of the contaminant in the dissolved phase. This is marked by the CSIA values getting much heavier for the dissolved contaminants. The second stage is dissolution of undegraded contaminant from the solid phase. This second stage can result in rebound and the CSIA values getting lighter and looking more reflective of undegraded contaminant. The third stage is the slow destruction of that desorbed contaminant. Here we see the CSIA values again getting heavier. If the injection is monitored only once, at a time well into the third stage, the effectiveness of the injection will be underestimated, as will the role of the contaminant mass on the solid phase. The first leads to the mistaken impression that the injection was minimally effective, and the second leads to an underestimate of just how much mass is stored in the solid phase. That underestimation could cause future remediation efforts to be undersized and far less than optimal. Injections of bioaugmentation/biostimulation amendments have an effective stage in which the CSIA values get heavier and an exhausted stage in which the CSIA values are constant. In simple systems contaminant concentrations generally decrease and CSIA values get heavier. However, varying flow conditions or the presence of NAPL may make concentration monitoring an ineffective tool for monitoring the onset of the exhausted stage. For optimal performance, semiannual monitoring is recommended to see if the amendment is exhausted. Less frequent monitoring can lead to longer periods between injections and longer cleanup times.

Because isotopic ratios can yield information about the presence of NAPL, it is possible to distinguish dilution from degradation. Isotopic ratios can provide information about the mechanism of that degradation. Optimization may include a stable isotope survey to test and/or refine the CSM. The specific design of the survey depends on the current CSM; however, to characterize the smallest sites, one sample for CSIA may be taken in each critical area of the site with a minimum sample size from four monitoring wells. The samples can be collected during a routine sampling event. This data set could then be used to determine if optimization decisions require more detailed stable isotope information in key areas of the site. For example, to better understand the nuances of which degradation mechanisms are active in each area of the plume or to see where undegraded contaminant mass is entering the dissolved phase, a comprehensive survey of CSIA across the entire plume is recommended (typically requiring 12–20 wells, depending upon the size and complexity of the site). CSIA surveys would be performed upgradient, in the source zone, along the center flow line and throughout the plume area, and include a vertical dimension (USEPA 2008). Both spatial and temporal sampling designs may be developed for CSIA surveys. This survey would inform optimization strategies and establish a baseline against which future monitoring results can be compared to assess progress.

4.4.5 Monitoring Data Assessment

Data evaluation and interpretation are key components to assess whether remedial objectives are being achieved and 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 evaluate data to establish whether progress toward objectives is being made, generally including updating the CSM, statistical analysis, and modeling, which can include predictive and validation modeling.

In reviewing or evaluating the adequacy of the performance monitoring data, the following questions should be asked:

- Are the correct media and zone of contamination being monitored?
- Are the monitoring locations in sufficient quantity and located at distances to allow reliable data to be collected regarding injection distribution and concentration reduction?
- Is the correct delivery mechanism being used to implement the technology?
- Are the COCs and all potential byproducts being monitored?
- What other parameters represent lines of evidence to support the remedial goals for the site in question?
- Is the current level of data collection sufficient to enable the performance metrics to be analyzed?

Performance parameter selection depends on the type of in situ technologies applied (for example, ISCO, bioremediation, etc.). The parameters to be monitored should coincide with the baseline sampling and with evaluating the end points. Performance data may include geochemical, hydrogeologic, and microbial data along with the evaluation of chemical, physical, or biological processes in the subsurface.

Tracking changes in geochemistry is also useful in evaluating the long-term effectiveness of a prescribed injection system. It is common to simultaneously evaluate geochemical parameters while performing groundwater monitoring events. However, geochemical parameters may be evaluated on a different frequency. Evaluating geochemical changes versus time can aid in evaluating the subsurface activity and distribution of the injected material. For example, a significant increase in methane concentration within the hot spot of a petroleum plume or after an anaerobic substrate injection would indicate an increase in microbiological activity in the affected area. Additionally, geochemical isopleths aid in visualizing the extent of an injection’s dispersion. Conversely, no change in geochemistry may indicate the injected material has not reached or sufficiently affected its intended target area. Other factors could contribute to system performance that does not meet design expectations. Please refer to Section 1.3 to identify a path forward once performance is deemed inadequate.

Performance monitoring is an iterative process and will need to be completed throughout treatment to provide information for optimization. These questions will provide a basis for this monitoring, and if inadequate performance is identified, the information in Section 2 can be used to evaluate next steps.

To assess overarching functional objectives such as exposure, extent, fate, and transport of COCs in a source zone or plume, as well as progress on remedial actions, SMART attributes (specific, measurable, attainable, relevant, and time bound see ITRC 2011c for a description of SMART objectives and the assignment of attributes) need to be assigned to the remedial objectives. This process will define a specific measurable quantity or metric for each medium to be monitored. When setting SMART attributes for the remedial action, each attribute should be considered and modified to be site-specific. The following provides an overview of key performance metrics to consider in setting up the monitoring program.

4.4.5.1 Concentration

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Contaminant concentrations in soil, groundwater, and soil vapor are used to assess the site's remedial progress and compliance. Screening values and numeric, chemical-specific remedial goals are typically concentration-based metrics used to evaluate compliance. An analytical value represents an average concentration in the media collected at the location and depth interval of the sampling device during the time of the sample collection. This is an important consideration given the role concentration data play in the decision-making process. A rigorous assessment of sampling methodologies, their influence on the sample results, and their relationship to the performance metric or remedial goal should be carefully considered in the monitoring approach. Bias in sampling methods (e.g. the effect of pumping rate on the groundwater sample, seasonal influence, etc.) should be recognized and mitigated or eliminated if possible.

Compliance monitoring data should be evaluated to assess trends associated with the remedial action. Isoconcentration plots are a common way to evaluate the data. Linear regression trends such as concentration vs. time and distance plots are also common means of evaluating data. However, statistical analysis such as Mann-Kendall should be performed periodically to determine if the trends are statistically significant, stable, or nonexistent.

In addition to the targeted COC, byproducts of the treatment should be monitored and evaluated during the postinjection sampling events. These byproducts or daughter products, depending on the remedial technologies used, should be evaluated to optimize treatment.

4.4.5.2 Mass

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Estimating the mass of a contaminant removed, reduced, destroyed, or remaining from a COC plume (source zone or downgradient plume) can be an effective way to evaluate system performance and assess potential exposure. An estimate of mass destroyed can be derived by calculating the total mass balance, including the degradation products, or measuring the difference between the initial and final aqueous mass. (ITRC 2010) pointed out:

"Many regulatory discussions about sites with groundwater contamination are driven by point-in-time measurements of contaminant concentrations 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."

Like concentration data, sufficient data should be available to estimate the mass of the contaminant. This estimate should encompass the area where the injection is expected to occur. These data will then be used to assess mass reduction after the injection delivery. Note that it may be very difficult to estimate the mass due to uncertainties in the contaminant distributions and the potential presence of NAPL; mass data should be carefully assessed to account for this uncertainty.

Using the performance monitoring data, the estimates of mass reduction can be made throughout the remedy implementation to assist in evaluating system performance and optimization.

4.4.5.3 Mass Flux/Discharge

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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 2010; ESTCP 2010b).

These estimates have limitations and inherent uncertainty. In fact, the uncertainty can be significant and should be quantified and considered relative to the typically more certain "concentration only" approaches. The degree of accuracy required for mass flux or discharge estimates should be selected based on remedial objectives (ITRC 2011c). Even with the uncertainty found in these measurements, mass flux and mass discharge data can help with the following:

- combine contaminant concentration and groundwater movement data
- quantify changes in contaminant mobility and movement over time
- enhance evaluation and optimization of remedial technology and system operation

In some cases, an initial rough approximation may be sufficient, while more accurate measurements are necessary to understand the value of continued remediation on mass transport.

Using the performance monitoring data, the reduction of mass flux/discharge from the treatment area can be made throughout the remedy implementation to assist in evaluating system performance and in optimization.

4.5 Implementation Optimization

Optimization improves the protectiveness and cost-effectiveness of remedial actions. This is consistent with the general definition given in the ITRC Remediation Process Optimization guidance document (ITRC 2004), which emphasized efforts to maximize protectiveness and minimize cost. As used in this document, optimization is defined in a more rigorous way, emphasizing the process to make remedial efforts "…as fully perfect, functional or effective as possible" (Section 4.4.2.1). Optimization can be quantitative (formal) or qualitative.

Agencies at the local, state, and federal levels and private sector have worked over the years to use optimization practices and come to a consensus on optimization lessons learned and optimization reviews and how they apply to ongoing environmental projects throughout the regulatory process for the benefit of all. Where applicable, optimization stakeholder meetings and other aspects of optimization activities may be considered (USEPA 2013).

4.5.1 Formal Optimization Techniques

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Employing formal optimization techniques can help to find the optimal conditions or actions that minimize time or cost for remediation subject to project constraints (for example, budget, plume extent, physical limitations). These techniques are usually coupled with some type of simulation software that predicts the future state of the system given various chemical, hydraulic, and physical input parameters. The formal optimization techniques explore potential actions that result in cost reduction or time reduction to attainment of a remediation goal (for example, concentration or mass discharge).

For in situ remediation technologies, the optimization tools simulate the impact of change on the remediation. The optimization tools would allow a determination of the optimal spacing, timing, and quantities of amendment, as well as the optimal transition points in a treatment train approach, or transition to MNA, to minimize cost or time for remediation. These methods can also determine a trade-off curve to find a most favorable combination of effort, cost, and time.

Work on the application of these techniques specific to in situ remediation, including the use of amendment injection, has been sponsored by the Department of Defense Strategic Environmental Research and Development program (SERDP) and conducted by Dr. J. Parker and colleagues (Parker 2011). The demonstration sites used in the SERDP projects have included injection technologies and considered the optimal injection programs, as well as the transition in time and space from one technology to another. The work also evaluates the uncertainty in the *optimal* approach.

Another related effort funded in part under the Department of Defense Environmental Security Technology Demonstration Certification Program (ESTCP) was the development of the PREMCHLOR tool that allows a probabilistic evaluation of the effect of uncertainty in the site and design parameters for source and dissolved plume remediation (ESTCP 2011a). The report is freely available, as is the code.

ESTCP project ER-200318 (ESTCP 2011b) Final Report-Fort Lewis Diagnostic Tools for Performance Evaluation of Innovative *In situ* Remediation Technologies at Chlorinated Solvent-Contaminated Sites. The report includes performance criteria and recommended use along with technology costs for 3-D sampling of multiple level wells, CSIA, molecular diagnostic tools, and mass flux analysis. The report explains how molecular tools such as qPCR may be recommended for DHC and function genes, but not recommended for methanogens at most sites, while other specific molecular tools were not applicable

These tools may be particularly useful for large and expensive in situ remediation projects, but can be applied to sites of any size. The data needed to support these analyses may include the approximate unit costs for different actions or injection amendments, monitoring costs, and uncertainty estimates for contaminant extent or mass, effectiveness of delivery, etc. Observations from pilot testing may allow estimation of some of these parameters.

4.5.2 Optimization and Verification of Treatment Effectiveness

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The monitoring recommended for evaluating performance of the injection program should be used to assess the appropriate changes for additional injection events (ITRC 2011c; USEPA 2011b, 2018b). Although design, based on careful site characterization, would provide a starting point for the injection project, the observations of contaminant and amendment concentrations, groundwater geochemistry, hydraulic responses, and high-resolution profiling, etc., following initiation of the project allow an observational approach for optimization of the remaining project. In many respects, the initial injection event is an effort to validate the RDC and provide clues for optimization. Rarely are in situ treatment objectives met after one injection due to matrix back-diffusion, site heterogeneity, and delivery challenges. In fact, the first injection often leads to upsets and redistribution of contaminants. The areas and depths of the TTZ that do not respond to injection as anticipated are identified and addressed through a multistep process to optimize subsequent injection(s). In situ remediation commonly fails when the initial injection scheme is repeated, often to recoup the investment in permanent injection wells, rather than reacting methodically to what the performance monitoring data are telling us. The data following the initial injection event should be critically reviewed as if evaluating a pilot study.

Optimization follows a systematic process. First, the volumes that are inadequately treated, or that are unlikely to reach treatment goals within the targeted treatment times, are identified through the evaluation of the monitoring data, consideration of subsurface transport, and injection program performance (for example, volumes injected, refusal for direct push points, pressures used). The amendment concentration may need to be sustained, particularly with biological processes, for a long period of time to establish optimal conditions for remedial process (see Section 3.5). With ISCO applications the reaction may be occurring too quickly, which leads to costly waste of amendments. With other amendments, if the reaction occurs too slowly, amendments may be washed out of the treatment area by groundwater movement before an effect is observed. The three-dimensional extent of those problematic areas needs to be identified. Flow and transport modeling may be useful to assess areas that may not be adequately treated over time (see Section 3.5).

Second, the cause for the poor performance is identified. Hydrogeologic data, site history, geochemical conditions, and soil/rock physical properties should be evaluated and the CSM updated (see Section 4.4.2.1). Examples of the modifications to the conceptual model could include the addition of a new preferential pathway for amendments, lower permeability of target materials than expected, excessively high pressures used during injection, additional existing chemical/amendment demand, or inadequate microbiology. The analysis of the cause(s) of poor performance is best done by practitioners, in multiple technical disciplines, to ensure that all aspects contributing to the poor performance are identified.

Finally, optimization revisions are proposed for subsequent injections. Modeling may again be useful to support recommendations. The recommended optimization actions could address:

- changes in injection spacing, location, and depth/vertical interval
- changes in delivery method, including injection methods, pressures, rates of delivery, or use of permeability enhancement
- changes in amendment concentration, type, or mix (for example, activators, biological cultures)

The optimization recommendations are implemented and performance monitoring continued. The performance monitoring program itself may also be optimized based on the observed responses. Additional monitoring points or parameters may be added and the frequency of the monitoring itself may be modified—either increased or decreased. Monitoring locations may also be removed if in areas that have attained goals, or that are not functioning.

The optimization process may be repeated multiple times during the project duration. These modifications, if based on solid analyses, will reduce project costs and duration. A checklist for optimization of injection programs is provided as Appendix F to this document.

4.5.3 Changing Conditions

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More complex circumstances are those that are not expected; however, based on the experience of professionals working on similar projects, these circumstances should be considered in advance in the event a contingency plan is necessary to address these conditions. These situations should be evaluated as part of the remediation risk analysis and documented in the risk register or change management system. The mitigation measures for significant risks should also be documented. Note that some of the risks can and should be addressed with some preinjection testing or characterization. Below are some of the circumstances to consider and for which to prepare contingencies.

- The specified injection volumes take longer than expected, lower injection rates are required, or the injection plan cannot be completed at design pressures, resulting in lower injection rates.
- Daylighting of amendment occurs (for some applications, this has a high probability of occurring).
- Amendment does not propagate the expected distance or at the expected volume to achieve ROI.
- Oxidant demand is greater than anticipated despite bench testing on representative soils.
- pH drops substantially.
- Injection wells become clogged or the formation will not readily accept amendment.
- Amendment is diverted outside the TTZ (for example, vadose zone when the saturated zone was the target).
- Direct push technologies are not able to reach the design depths in portions of the site.
- Injection displaces the plume into previously unaffected areas.
- Mixing equipment malfunctions.
- Direct push equipment breaks down.
- Mechanical equipment and system infrastructure fail.

The mitigation measures or contingencies to be considered may include:

- increasing or decreasing injection pressures
- use of hydraulic or pneumatic fracturing emplacement
- routine rehabilitation program for injection wells
- availability (on site and contractually) of additional amendments and increases or decreases in volumes or concentrations
- adding injection points in between existing transects or wells
- assessment of alternative drilling methods and knowing the contractor can have the equipment with minimal delay
- enhancing transport through groundwater extraction and recirculation or operating in conjunction with phytoremediation for hydraulic control
- spare parts inventory available on-site during the injection process.

Other risks and contingencies would be site-specific, and the risk assessment method will help address these.

Based on results of the performance monitoring data, a remediation project may be able to transition to closure, MNA, or in some cases, an alternate remedy (Appendix E.7, Terra Vac under USEPA's Demonstration Program Conducted Soil Vapor Extraction (SVE) in the Source Area). In this subsection, both intentional and unplanned transitions are discussed. Keep in mind that for very large plumes, where in situ injections are performed as an interim measure as a part of mass reduction and overall plume management, this logic may not apply.

4.5.4 Subsequent Amendment Applications

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Planning for injection events subsequent to the initial event is typical for most in situ remedial technologies considering site heterogeneity and matrix back-diffusion and should be included in the implementation plan along with triggers for reapplication described in the monitoring plan. In most cases the additional injection events are expected and meant to address areas not fully dosed due to substantial demand for the amendment or incomplete contact with the contaminant due to site heterogeneity or dissipation of the amendment before the remedial objectives were achieved. In other cases, repeated injections are required to treat continuing contaminant mass flux as part of a barrier configuration or for treatment of mass discharge from an inaccessible source area (Appendix E.14, Naval Submarine Base, Kings Bay, Site 11).

In these situations, the locations and dosage of additional injection events are tailored based on monitoring results indicative of contaminant rebound or diminished amendment concentrations. Other modifications could include tailoring the mix of amendments to adjust to other observations, including microbial populations, pH, DO, and ORP. Both schedule and budget for the project should be developed accounting for these potential needs. For instance, as a cost-saving measure, analysis of microbial populations at a bioremediation site is not conducted until the data indicate that reactions are not going to completion despite the presence of adequate electron donor and ideal geochemistry, as demonstrated by lower cost analytical parameters. At this time, it is beneficial to invest in microbial analyses to evaluate optimization of the remedy through bioaugmentation.

In most in situ injection applications, it is not uncommon to see more than one application of amendments for the successful treatment of subsurface contamination. Amendment applications are often designed to be multi-injection events and are planned and funded accordingly. Sometimes subsequent injections are necessary based on the conditions observed in the site as a result of initial injections. Insufficient understanding of the site-specific conditions may result in improper and ineffective amendment applications, which will result in not meeting the intended goals, exceeding time to completion and cost to completion estimated in the planning stage.

Subsequent amendment applications can be planned and performed in many ways. Some of the approaches for these applications include:

- division of the plume into areas of priority to implement injections in a systematic manner (for example, cut-off zones)
- targeting areas where baseline concentrations were higher or the ROI was limited versus a shotgun approach where more amendment is needed in treating the entire area
- changes to the amendment formula to include nutrients, microbes, pH adjustment, or activators
- application of different amendments to address daughter products (for example, emerging contaminants) or byproducts that may require different processes to successfully meet the goals for all constituents
- vertical and horizontal isolation of target areas for maximum effectiveness
- limits on the maximum dosing of amendments or total volumes that can be injected during a single event

In many cases, subsequent applications are necessary as a consequence of changing site conditions, which were not originally anticipated.

4.6 Transition and Contingency Planning

Two types of conditions have been identified to require transition and contingency planning: anticipated subsequent application events that are commonly included with in situ injection programs (for example, ISCO), and unexpected conditions that may occur related to injection events. Both conditions are addressed with the suggested contingencies. The practitioner must consider the risk of these conditions for the site during the planning stage of the project and develop contingencies for those risks so a contingency plan can be implemented quickly.

When the risk justifies it, a mitigation or contingency strategy is developed. This risk management approach is outlined in Project Risk Management for Site Remediation (ITRC 2011d). The approach involves the preparation of a risk register that summarizes the various risks and their likelihood and impact. If the risk is small (highly unlikely or very minor impact), the risk can just be accepted. If the risk is substantial (likely occurrence and significant impact on cost and schedule), then there should be a plan to address this if the condition occurs.

4.6.1 Intentional Transition Planning

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Naval Submarine Base Kings Bay Site 11 has used pump and treat—in situ chemical oxidation—biostimulation—monitored natural attenuation (NAVFAC 2013a) Since 1999, two long-term monitoring programs have been conducted at Site 11, including monitoring as required by the RCRA permit, and performed in accordance with the associated groundwater monitoring plan (GWMP) (Bechtel 1999), and monitoring conducted by the U.S. Geological Survey (USGS) in coordination with the Navy to

Closure is perhaps the easiest transition to make because it assumes all monitoring wells or sitewide average concentrations meet the remedial action goals set by the lead regulatory agency and maintained those water quality goals for a specified duration. Once these criteria are met, the regulatory agency can grant closure. As a precaution, it is recommended that the CSM be thoroughly reviewed to verify that the monitoring well network adequately evaluates the vertical and lateral extent of previously affected areas. Once all regulatory requirements have been met and closure is granted by all regulatory agencies, be sure to properly abandon all remediation infrastructure and monitoring wells.

Many sites where in situ injections are performed will transition to MNA (see Section 3.2.3). Before ceasing active remediation and transitioning to MNA, develop an accurate estimate of how many years the project will be monitored and prepare a cost-benefit analysis of MNA compared to additional active remediation, recognizing the potential limitations for active treatment of residual mass. While logical and enticing to terminate active remediation, MNA guidance is prescriptive and can be expensive to follow. In many cases the life cycle cost of a remediation project can be reduced with additional targeted active remediation. In other cases, the technology has accomplished significant reduction in contaminant concentration and the residual impacts will naturally attenuate at approximately the same rate as would continuing active remediation. Review figure 2-1, expanded MNA/EA decision flowchart, (ITRC 2008a), for the use of monitored natural attenuation and enhanced attenuation at sites with chlorinated organic plumes in Performance Assessment for Pump and Treat Closure or Transition (PNNL 2015), and other guidance appropriate for other site-specific constituents of concern and individual state guidance to verify that the site is a candidate for MNA. Furthermore, review the CSM to verify that the monitoring network adequately evaluates the vertical and lateral extent of the residual impacts. Abandon wells that are no longer necessary and replace wells that have been damaged or need to be relocated to allow for development of the site.

evaluate the effectiveness of natural attenuation processes in reducing contaminant concentrations (USGS 2009). The RCRA permit required that monitoring begin in 1999, and the monitoring program was adjusted several times based on the exit strategy provided in the GWMP and other recommendations from the Georgia Environmental Protection Division. The USGS monitoring was conducted from 1999 to 2009 at a number of designated wells. The study confirmed the effectiveness of natural attenuation processes at Site 11 (USGS 2009). After the completion of the USGS study, these USGS monitoring wells were not sampled in 2010. Groundwater was sampled in 2011 and a new sentinel well was installed in 2012. Optimization reports have been performed and the site is currently under a monitored natural attenuation phase.

For a statistical approach, refer to “An Approach for Evaluating the Progress of Natural Attenuation in Groundwater (USEPA 2011a). (ITRC 2016, 2013b) use a regression analysis or nonparametric analysis such as Mann-Kendall (for example, MAROS or ProUCL). Numerical reactive transport modeling such as RT3D (Microsoft Excel-based platform) provides a tool with which to quantify the relative stability of a contaminant plume, particularly in cases where simpler evaluations are not suitable because of complex hydrology, past activity at the site, multiple contaminant sources, and/or complex reaction of multiple species (Johnson 2006). Selection of an appropriate model configuration to represent spatial and temporal variations in site-specific attenuation processes can facilitate assessment of the contaminant loading and attenuation capacity (that is, mass balance) at the site.

In some cases, the remedial action plan includes a treatment train. A treatment train may be necessary for large plumes or those with extremely high concentrations in the source area, whereby a more cost-effective remedy can be implemented once an interim remedial goal is reached. In other cases, the daughter products or residual constituents are more effectively treated using a different technology. For example, in situ thermal remediation may be used to reduce NAPL or high concentrations in the source area quickly. However, due to high operating costs and the lateral extent of the plume, it is more cost-effective to treat the downgradient portions of the plume with EISB or heat-activated persulfate. Many potential combinations of remedial technologies are effectively used in tandem (see table 4-1 in (ITRC 2011c)). The metrics and decision points for the transition should be clearly identified. The metrics may be concentrations, concentration trends, or mass flux/discharge. Be mindful that not all technologies are compatible. For instance, if a source area is treated using ISCO, the area may be too oxidized to effectively and efficiently follow with an anaerobic EISB to achieve cleanup criteria unless large doses of substrate, pH adjustment agents, and bioaugmentation culture are injected. As a result, it would likely be effective to implement an anaerobic EISB to remediate groundwater impacts downgradient of a source area that was treated with ISCO. For more discussion on treatment trains and technology compatibility, review chapter 4 of (ITRC 2011c).

4.6.2 Contingent Remedy Transition Planning

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In cases where the initial remedial technology fails to achieve the desired goal, an alternate remedy must be implemented. Many Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA/Superfund) sites include an alternate remedy in the record of decision (ROD). However, as technology advances, the approved remedy and the alternate remedy may no longer be the best technology for a particular site and reopening the ROD may be the most cost-effective and appropriate outcome for a site (Appendix E.11, Eastern Surplus Company Superfund Site). Depending on the factors that limited the effectiveness of the selected remedy, an alternate in situ remedy may not be appropriate. For more discussion on remedy evaluation, review chapter 6 of (ITRC 2011c).

The criteria for transitioning to the alternate remedy is often poorly defined. Statistical evaluation of performance monitoring data using a regression analysis or nonparametric analysis such as Mann-Kendall (MAROS or ProUCL) is commonly used to determine if the remedy is performing (see Section 4.6.1 for more examples and references). If there is a trend in performance monitoring data immediately downgradient of the treatment zone, but no significant trend observed farther downgradient within the modeled time frame, several things could be happening.

- The remedy may need more time to respond because the retardation of amendments in the aquifer matrix was not fully understood.
- The advective transport velocities may have been overestimated.
- There may be additional source materials that were not addressed by the prior treatment.
- Back-diffusion may provide a persistent source of COCs from less mobile portions of the aquifer or partitioned mass may require significant time to become available for treatment through diffusion.
- If ISCO was used, it could be that the native organics were oxidized before the anthropogenic organics, and there is not enough oxidant to effectively treat the COCs.
- There could be a preferential pathway through which the amendments traveled, and distribution of amendments throughout the area of concern could not be achieved.

See 4.4.1.3 for a list of common issues encountered during implementation and postimplementation monitoring of in situ treatment technologies. This table provides links to additional information within this document or external citations or web links for guidance on a wide variety of in situ technologies, amendments, emplacement technologies, and monitoring protocols. Revisit the CSM for the site and update it to include all new information learned during implementation of the initial in situ remediation technique.

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5 Regulatory Perspectives

In addition to the technical challenges encountered during the design and implementation of in situ remedies, environmental statutes and their implementing regulations may also pose obstacles to the implementation of in situ remedies that make success more uncertain. The goals of this section are to identify statutory and regulatory challenges and to suggest ways to address them to improve the chance of success.

5.1 Statutory Challenges

Site cleanup activities are governed by multiple statutes and regulations. Many remediation sites are regulated under either the federal CERCLA or RCRA processes along with state requirements. Sites that do not fall under federal CERCLA or RCRA oversight are regulated solely through a state or local regulatory process. Additionally, federal requirements mandated by the Clean Water Act (CWA) and Safe Drinking Water Act (SDWA) may apply, depending on site conditions and the remedial approach.

Specific CWA requirements that may be applicable to in situ remediation include, but may not be limited to, UIC permits and antidegradation policies and requirements. SDWA requirements may apply to proposed amendments that have the potential to cause exceedances of primary or secondary drinking water standards (e.g., MCLs).

> Antidegradation requirements can place limitations on the use of an amendment itself, or secondary products. Both affect the implementation of the proposed remedy. For example, in situ chemical oxidation can cause the generation of hexavalent chromium, which needs to be controlled.

Each state may have specific regulations governing the placement of amendments into the subsurface. State regulations may limit the types and quantities of amendments; require permitting, approval or contingency plans; or prohibit some types of hydraulic fracturing. States may also have anti-degradation policies. Various county or city ordinances may also apply.

Federal, state, and local requirements may add time to the approval and implementation of the cleanup process but are meant to ensure the protection of human health and the environment. A thorough review of all site-specific permitting and regulatory approval requirements is necessary before preparing plans to implement or modify in situ remedies.

An understanding of potentially applicable requirements early in the cleanup process is critical to timely approval and implementation of an in situ remedy. When an in situ technology is first identified as a viable remedial option, communication between stakeholder, practitioner, and regulator is needed to identify what submittals are required prior to implementation (that is, UIC permits). Timely communication with the regulatory agencies overseeing the cleanup will assist with regulatory compliance and regulatory and stakeholder acceptance.

5.2 Traditional CERCLA Site Cleanup Process

5.2.1 Historical Process

CERCLA, later amended by the Superfund Amendments and Reauthorization Act (SARA), and its implementing regulation, the National Contingency Plan (NCP), established the CERCLA process for addressing potentially contaminated sites. Although cleanups under RCRA differ somewhat, the process for National Priorities List (NPL) sites (whether the cleanup is led by the federal government or a state), as well as for many state programs, is often applied to complex sites where in situ remediation is used.

The CERCLA traditional process is largely linear, starting with preliminary assessments, and if a site is listed on the NPL, continues with site investigations, remedial investigations, and feasibility studies. Once a need for remediation is determined, several technologies are evaluated. The record of decision (ROD) documents the selected remedial technology and approach. This process is shown in Figure 5.1.

Early actions can also occur at any point in the process. These include emergency responses or interim remedial actions. Early actions are meant to reduce risk quickly, control groundwater plume migration, or facilitate site reuse (USEPA Memorandum “Use of Early Actions at Superfund National Priorities List Sites and Sites with Superfund Alternative Approach Agreements,” 8/23/19).

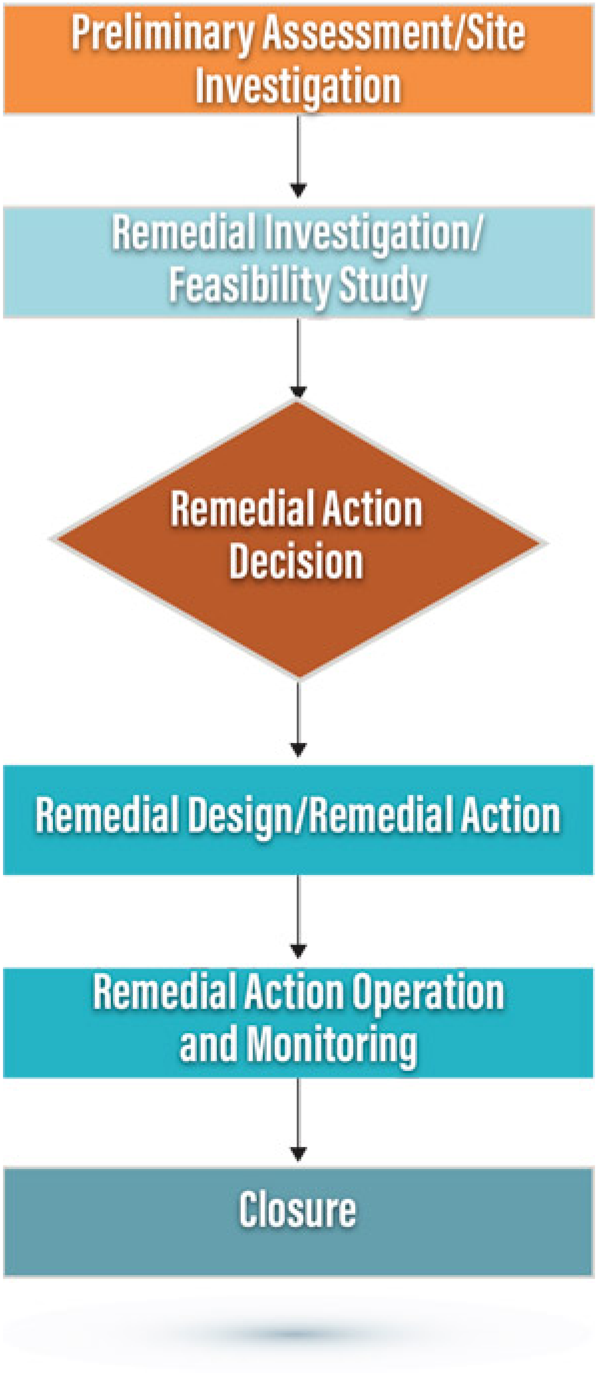

Figure 5.1. Traditional regulatory processes.

However, the overall process generally follows a linear order of tasks meant to result in a final site cleanup.

If the initial approach to cleanup specified in the ROD is not effective or feasible, remedial options can be reevaluated and then modified in a Record of Decision Amendment (RODA) or Explanation of Significant Difference (ESD). This process to document remedy changes, while needed for many reasons, can cause significant delays in completing cleanup.

With respect to in situ treatment, the remedy in a ROD or RODA may be too specific. For instance, decisions may have specified the amendment, method of delivery, or both. In these cases, if during design or implementation a change in either of these remedial approaches is identified, it would require a time-consuming change to the decision document.

A more effective approach could be to select a more general class of remedy, such as ISCO in general rather than a specific oxidant. Although the feasibility study would base the evaluation of ISCO on the performance data for specific oxidants used at other sites, the selection of the amendment could be made in design. Similarly, the application method can be left to the design phase rather than described in the decision document. Also, depending on the uncertainty associated with an in situ approach, the decision can include a contingency remedy that has been fully evaluated and could be used in lieu of the first remedial choice.

One way regulators try to mitigate the risk of an ineffective remedy is to require a high threshold of information before a decision is made. As discussed earlier in the document, optimizing the application of in situ remedies is complex and requires iterative testing and adjustments within the individual steps, such as remedy design. In situ treatment pilot test results, or initial monitoring of a remedy, may show that the original amendments or delivery method were not functioning as expected. The challenge is allowing sufficient flexibility in the remedy decision to develop an appropriate in situ approach while allowing for the uncertainty of success through contingency strategies.

To advocate for a more flexible approach to the remedy in a decision, convey to the regulator and other stakeholders the iterative nature of the design and operation of in situ remedies, particularly those using amendments, This communication could occur during review of an in situ treatment proposal (work plan) that includes the iterative testing and implementation process described in Figure 1-2. The need for later revisions will be minimized if this iterative process is built into the decision and implementation documents. These documents can be flexible with respect the amendment, amendment dose, or delivery method.

5.2.2 Survey Results

The ITRC In Situ Optimization Team developed a survey (Appendix G) to identify regulatory challenges to implementing in situ remedies. The survey was widely distributed to ITRC members. The purpose of the survey was to determine how many in situ projects the respondents had been involved in, evaluate the rate and root causes of why any of the proposed projects were initially not acceptable to the regulators, and identify common reasons for this occurring. The ultimate goal was to find areas where regulatory impediments could be addressed to help reduce uncertainty in implementing in situ remedies.

Although the survey results showed that practitioners and regulators review about the same number of in situ proposals, the regulators were approximately 40% more likely to deem the first submittal as incomplete.

5.2.2.1 Reason(s) for Incomplete Submittal Determination

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At a similar frequency, both practitioners and regulators identified that an inadequate CSM in the initial submittal caused the submittal to be deemed incomplete. The areas where submittals were found incomplete by regulators at a higher rate than the practitioners were: (1) the assumptions used in the CSM or remedy design were not clearly described in the narrative; (2) the proposed in situ treatment method was questionable (e.g., ISCR vs. ISCO); and (3) the proposed amendment was questionable.

5.2.2.2 Root Cause(s) for the Inadequate Information Provided

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The areas within the CSM that regulators identified as incomplete at a higher rate than practitioners were: (1) inadequate proposed placement of the amendment based on the CSM; (2) the data did not support the ability of the proposed remedy to reach remedial action objectives (RAOs); and (3) the effectiveness of the proposed amendment was questionable.

The survey data also indicate that the regulators' expectations for sufficient documentation regarding the proposed in situ remedy are not being met with the initial submittal. The root cause analysis portion of the survey shows that before they will give regulatory approval the regulators want a more detailed description of the assumptions that form the basis for the proposed remedy; justification of why the amendment selected is the most appropriate based on site-specific conditions; and discussion of how the remedy will comply with requirements and achieve RAOs and how the proposed in situ treatment compares to other in situ technologies,.

5.2.3 Challenges with the Traditional Regulatory Approach and In Situ Treatment

The interpretation of the survey results in Section 5.2.2 indicates that regulators generally want more information to support an in situ remedy than is often provided by the practitioner in the first submittal. In the traditional approach the regulator tries to mitigate risk by requiring a high threshold of information needed before a decision is made. Frequently the regulator would require more investigation, bench studies, and/or pilot testing to refine the CSM and demonstrate that the proposed remedy is more likely to be successful than other remedial technologies.

This process would lead to a very specific description of alternatives that would then be incorporated into the site's decision document. The implementation of these highly prescriptive decision documents often become drawn out because administrative changes to a decision document are difficult and time-consuming. To overcome delays, regulators and practitioners should:

- identify decision points in the process when consensus on a path forward makes sense within the context of Figures 1-1 and 3-1 within the staircase diagram, define where regulator review/approval is required under a given program (that is, necessary or decision document and final full-scale Remedial Action (RA) following bench/pilot)
- use the general technology proposed (that is, in situ remediation), but specify actions that must be done to address uncertainties (for example, need pilot test)
- consider which "boxes" in Figures 1-1 and 3-1 require public notice

In 2018, EPA's Office of Superfund Remediation and Technology Innovation issued a memorandum to Superfund national programs managers USEPA Superfund Task Force #3: Broaden the Use of Adaptive Management. The purpose of the memorandum was to provide a working definition of "adaptive management" and to outline an implementation plan to expand the use of an adaptive management process at Superfund sites to improve and accelerate the cleanup process.

Figure 5-2 shows how an iterative process similar to that discussed in Sections 1, 3, and 4 (see Section 3.1, Implementation and optimization staircase) of this document can be used in the regulatory approval process for in situ remedies.

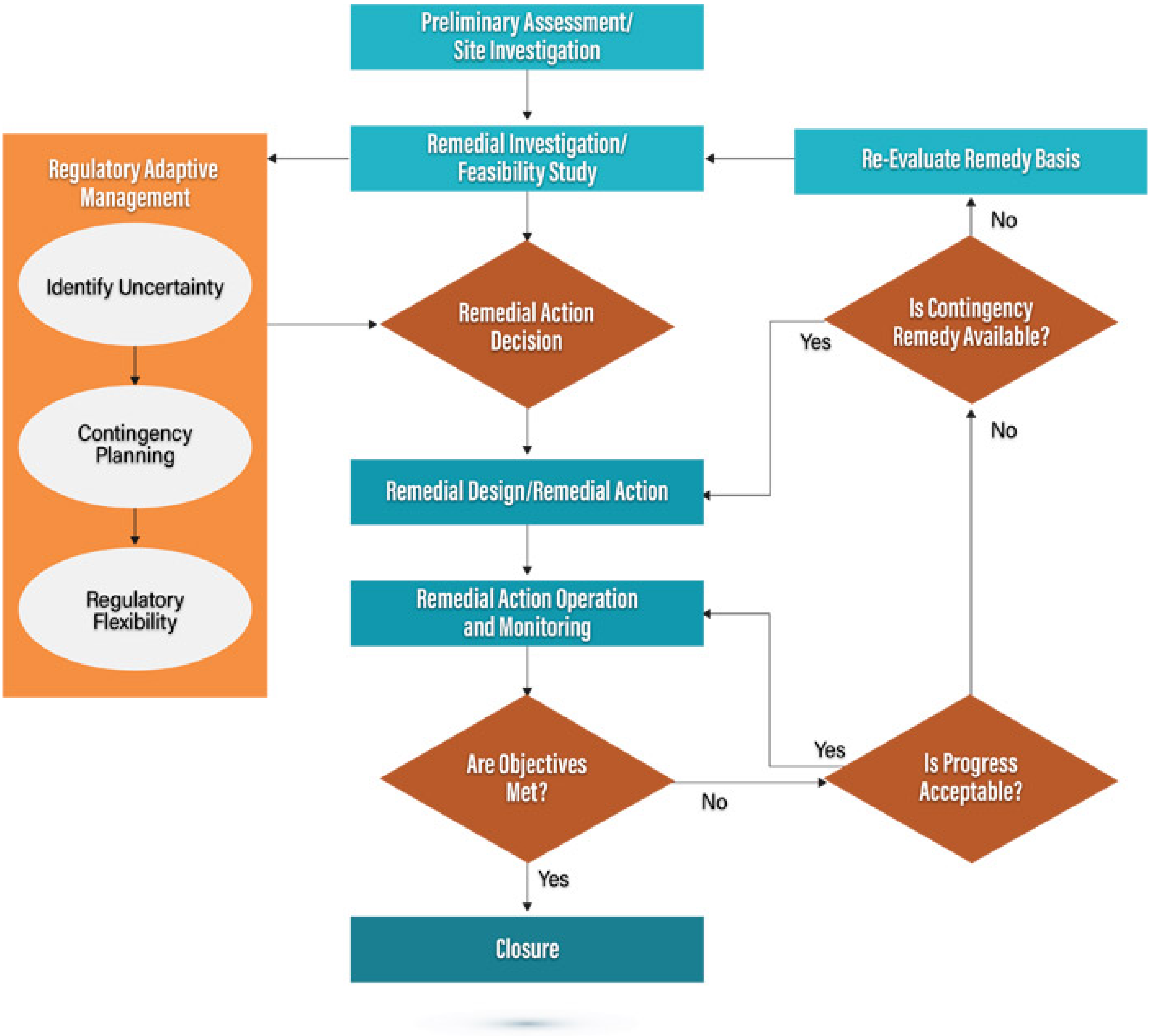

Figure 5-2. Regulatory adaptive management.

Understanding that the successful application of in situ technologies is an inherently iterative process, that the regulatory process can allow for iterations within the traditional regulatory process, and that the early and close coordination of all stakeholders is essential, it is possible to optimize the regulatory process by building needed flexibility into a project's decision documents.

The goal of regulatory adaptive management is to transition away from the traditional high threshold of information needed prior to the decision document to a regulatory environment that identifies uncertainties and provides robust contingency planning within the decision document itself.

If the decision documents to be implemented acknowledge the uncertainty and develop robust contingencies during the planning process, decisions can be made with significant uncertainties as long as it's clear how those will be managed and how decisions/changes in the remedial approach will be implemented.

When documenting the uncertainties and making contingency plans with respect to the use of different amendments, specific attention must be paid to the general type of amendment to be used (e.g., biotic (aerobic/anaerobic), abiotic (oxidizing/reducing), or a different kind of surfactant). If the change in amendment will change the geochemistry, different secondary effects (see Section 3.2.2) may need to be considered along with changes in the process monitoring (Section 4.4.1) A good example is moving from bioremediation to chemical oxidation or chemical reduction. This may require additional bench-scale testing. If well documented as a contingency in the original decision document, it may be possible to avoid additional authorizations and changes to the decision documents.

The amount of flexibility allowed in a decision document pertaining to the delivery of the selected amendment may also be constrained. For example, extraction and reinjection of contaminated groundwater can pose challenges, although (USEPA 2000) clearly stated that addition of an amendment that will result in treatment meets the requirement that contaminated groundwater be treated even if that treatment occurs after reinjection, or that hydraulic or pneumatic fracturing may not be allowable. Flexibility for the dosing of the selected amendment generally doesn’t need much documentation; it’s expected that additional rounds of injection are to be needed.

6 Community and Tribal Stakeholder Considerations

The implementation of in situ remediation techniques can be controversial due to community and tribal stakeholder perspectives based on a varied understanding of site characterization and in situ remediation technologies. Unlike ex situ remediation, stakeholders do not observe truckloads of contaminated soil being removed or *clean* water being discharged after treatment. Progress is not readily apparent and can be difficult to assess, particularly to the nontechnical stakeholder. Conversely, there may be less community resistance given that the remediation is less visible. If trust issues are present, gaining acceptance of the remedial action by the community is challenging, particularly during the optimization process when unforeseen deficiencies in the original design may be identified or changes in site conditions that affected the remediation become apparent.

Stakeholders benefit when they can influence remedy selection and long-term site management. Informed, constructive stakeholder involvement can assist in the decision-making process; reduce the likelihood of costly, time-consuming repeated work; and allow those in affected communities to have input into the long-term use of land, water, and other resources. If involved in the original decision-making process, community and tribal stakeholders will want to be informed on progress and potential optimization strategies throughout the cleanup, especially when progress is not satisfactory.

Various federal government, state, and sovereign tribal nations’ environmental statutes, ordinances, and acts require coordination with stakeholders and a reasonable opportunity for meaningful involvement in a project. Early and effective engagement can address concerns and educate stakeholders on the benefits of the site-specific in situ remediation technique. Communications with stakeholders can be used to:

- provide the public the opportunity to give comments and input to technical decisions
- inform the public of the remedial action progress and proposed optimization changes
- identify and resolve conflict

Specific guidance regarding relations with stakeholders is often provided by the project oversight agency, such as USEPA, DOD, or state regulators. These sources should be consulted for applicable procedures for community communication plans and minimum requirements.

6.1 Background

“Institutions never remember, but communities never forget.”

Stakeholders often have valuable information about site characteristics, history, and future site use that can improve the quality of remediation process decisions. It is often said that institutions never remember, but communities never forget. Although the focus is on a primary remedy selection, follow up and optimization are often done by people whom are less familiar with the entirety of the situation than stakeholders who have been involved from the outset. This is particularly applicable in tribal situations where projects often depend on external funding sources and varying political will, and suffer from extremely high rates of staff turnover. The project benefits from the careful explanation of findings and proposals that may be needed and the extra work needed to resolve site issues raised by stakeholders. Informed stakeholders are likely to be more be open-minded about optimizing in situ technologies. This is particularly important during the implementation process, when performance issues of the original in situ remedy design are discussed and a range of suitable adjustments is evaluated.

Each project and project site is unique in the appropriate level of stakeholder engagement for optimization of in situ treatment. The engagement of stakeholders depends on many factors. Local regulatory requirements will dictate minimum requirements. Beyond that, judgment should be applied considering:

- degree of community and tribal stakeholder involvement in the original remedial design and implementation
- technical issues that prompted the optimization review, such as:
    - failure of original system to treat contaminants to specified standards
    - mobilization of new contaminants not previously anticipated
    - expansion of the groundwater plume
    - potential impact to natural resources not previously identified
    - revisions to reduce schedule and costs
- permitting and public notification requirements
- impact on local community and economy issues (for example, extended schedule, newly defined areas of concern)

After these and other site-specific factors are identified and evaluated, the appropriate approach to stakeholder involvement can be developed.

6.2 Identifying Stakeholders

ITRC public and tribal stakeholders serve as the voice of the people who are most affected in their daily lives by the problems at hand. Stakeholders add key voices, as well as balance and diversity. They provide written and verbal input on a regular basis and in accordance with the team’s project work plan schedule.

The list of the site-specific stakeholders should be continually updated. Tactics for communicating the appropriate information to the audience should be considered. Tracking communications with stakeholders ensures that notifications are issued in a timely manner and that the appropriate parties are contacted. Clear communications are critical in moving the project forward and making adjustments where appropriate.

6.3 Stakeholder Concerns

Typical concerns of stakeholders revolve around how the changes in the remedial approach directly affect them or their constituents.

Understand Stakeholders’ Technical Backgrounds

At a former chemical plant Superfund site in New Jersey, local residents who attended public meetings included Ph.D. chemists (former employees) as well as nontechnical residents.

The following issues should be considered prior to communications with stakeholders:

- technical rationale for changes/optimization of an ongoing remediation
- public and tribal perception regarding changes/optimization
- regulatory impact/changes to permit conditions and reporting
- how changes will affect groundwater (for example, negatively—secondary contaminants could be mobilized, expansion of the plume, etc., and positively—treatment/capture of additional contaminants, reduction of chemical injected to the environment, etc.)
- the impact on the schedule (for example, will optimization accelerate the remediation or extend it?)
- appropriateness of public meetings (content and frequency)

Each issue could present different concerns, depending on the perspective of the stakeholder. For example, extending the schedule could be a concern to the public for local issues such as potential exposure or impact to business. For this reason, it is important to identify and understand the motivation, specific interests, and level of technical comprehension of each stakeholder. In cases involving in situ remediation on tribal lands, usual and accustomed areas, and ceded territories, it is important to realize that the cultural identity of the residents depends on the land. For example, as U.S. citizens, tribal members can assume that identity anywhere in the 50 states and live like a U.S. citizen. As a member of the Sac and Fox Nation, there is only one small place where that community exists. Remediation selection should look beyond standard health-based risk assessments to include factors that define a tribal community's identity.

Topics that stakeholders tend to raise typically relate to individual effects to the local population and environment, including effects on:

- health
- cultural practices and traditional lifeways
- property values
- jobs and tax revenues
- local businesses
- traffic, noise, and odors
- schedule and duration of remedial activities
- natural resources damage

The level of stakeholder participation and the appropriate process for the inclusion of stakeholders must be tailored to each site and situation; however, from the formulation of the problem through the exit strategy, stakeholder issues, needs, and concerns must be taken into account.

Stakeholder concerns that may arise during the implementation of optimization are discussed below.

6.3.1 In Situ Remediation Mechanics

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One benefit of in situ treatment is that it usually destroys contaminants rather than transferring them to another medium (for example, air, activated carbon). Stakeholders may focus on the following elements of in situ remediation techniques and processes.

- The public will question fracturing due to the negative publicity of oil & gas *fracking* and misunderstanding of its use in association with remediation. Explaining why this tool is appropriate and does not have the same consequences as in oil and gas applications is important.
- With ISCO, concerns may include creation of hexavalent chromium Cr^{6+}, creation of volatile vapors or explosion hazard potentials, appearance of daughter products, mobilization of previously bonded contaminants such as arsenic, daylighting of chemicals, odor, discharge to nearby streams/wetlands, and potential hazards to personnel and the environment when mixing.
- Concerns with in situ bioremediation generally include methane production, particularly in densely populated areas.
- The length of time to achieve remediation goals relative to ex situ technologies, and the understanding that MNA may be a component of the final remedy.

Process questions may arise on pilot and treatability studies regarding timing of completion, application to other areas, and full-scale design, construction, and operation.

6.3.2 Benefits and Risk

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The benefits of the proposed optimization process should be clearly stated as well as the potential risks. Transparency in communicating both the benefits and risks assists in establishing and maintaining trust with stakeholders. Ignoring or omitting potential risks can lead to difficulty in securing public concurrence and cooperation and complicate continued public cooperation during the optimization phase.

6.3.3 Changes in Site Conditions

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If the proposed optimization process will potentially result in changes to the site conditions that were not previously considered, these should be noted. Procedures to mitigate negative impacts due to changing conditions should be developed and presented to the stakeholders.

6.3.4 Potential for Direct Human Exposure

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Stakeholders will be concerned about any potential for increased exposure due to proposed optimization techniques. Nearby environmentally sensitive receptors, such as residences, schools, and childcare facilities, should be clearly identified on a figure. Discussions of the process used to identify the sensitive human receptors and to ensure protection from increased exposure should be included in stakeholder communications. The routes for potential exposure to consider include direct contact with:

- groundwater/supply wells
- soil
- surface water/sediment
- vapor intrusion
- subsistence and cultural hunting and gathering in potentially impacted areas

Each of these potential receptor pathways should be evaluated during the optimization process and results communicated to the stakeholders.

6.3.5 Potential for Indirect Exposure

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Stakeholders are concerned about all environmental pathways and may not accept excluding pathways such as ingesting homegrown vegetables irrigated by potentially contaminated groundwater. For example, if contaminants could be absorbed through the roots of plants, then this pathway should be addressed. The potential impact on local irrigation wells should be included in the evaluation of the local receptors.

6.3.6 Ecological Receptors

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Stakeholders may be concerned that the proposed optimization process could affect ecological receptors. Contaminants at levels well below cleanup standards appropriate for human health may present a risk to ecological receptors. For example, altering the composition of the media being injected could mobilize organic or inorganic elements that would not affect humans, but would affect water column species and/or wildlife, directly or through biomagnification (food chain toxicity).

Tribes and local sportspersons may be particularly concerned about addressing ecological receptors due to impact on fish and wild game.

6.3.7 Public Perception of Hazard

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If contaminants are in the news as a national threat to human health (such as lead in drinking water and household paint), the science behind in situ treatment may be outweighed by negative public perception of the hazards. The stakeholder perception of the site contamination should be considered in the decision-making process for optimization. Further education of the public may be necessary to gain stakeholder acceptance.

6.3.8 Remediation Progress

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As noted before, the progress of in situ remedial actions cannot be readily observed by stakeholders as can ex situ remediation (for example, soil removal). Consideration should be given to providing details on the monitoring plan, including sampling locations, frequency, and analytical parameters. Emphasis on sampling and analysis to confirm that the remediation is complete will provide stakeholders with a level of comfort that the project will not be declared complete prematurely.

6.3.9 Specific Tribal Stakeholder Concerns

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Tribes share many concerns with other stakeholders; however, they differ from other stakeholders in several key aspects. The 567 Native American tribes recognized by the Bureau of Indian Affairs are each culturally, governmentally, and socially unique.

Some tribes view any level of contamination of their land and natural and cultural resources as unacceptable. Many tribes have culturally significant or sacred areas, which may include springs, mountains, hunting areas, plant-gathering areas, or burial sites. When culturally significant or sacred areas are at stake, traditional methodologies that nontribal environmental professionals rely on (such as the applicable exposure scenarios, pathways, or factors for a risk assessment) may be superseded. Some plants and animals can also have tremendous cultural or religious importance to a tribe, including birds and feathers, game animals, herbs, grasses, and trees. These areas, items, and living things may be used in ways that are not addressed in standard risk assessment scenarios. There is also the potential for tribes not to disclose the exact location of sacred areas to outsiders, and in these cases there will be a need to work very closely with tribal members to explain to them the nature and extent of the remedy so that they can be assured these sites are not negatively affected. In addition, the exposure scenarios, pathways, and factors used in the risk calculations for tribal activities may differ from the USEPA or state default values. These values should be considered initially and reviewed again in the optimization phase of the project.

Tribes are sovereign entities that have established government-to-government relationships with federal, state, and local governments that must be recognized in the decision-making process. When a site affects a tribe, the project timeline must include tribal approvals in addition to other applicable agency approvals. Sampling, research, and services on tribal lands generally require institutional review board (IRB) or tribal council approval. Each sovereign nation operates differently, ranging from tribes that have no research capacity to tribes that have a full review board with a formal application process. The initial steps in the approval process may include drafting a proposal, preparing a poster or podium presentation, and presenting to the tribal government.

Once tribal approval is granted and the project commences, the practitioner must obey tribal protocol with respect to cultural practices. The tribe may reserve the right to retain the findings in the case of exploratory research and restrict publication. Regulatory findings for water and soil concentration, level of treatment, and monitoring are first reported to the tribe’s department of environmental quality or natural resources and then forwarded to USEPA.

6.4 Approach to Stakeholder Engagement

All interested stakeholders must have access to critical information and the opportunity to provide input to technology development decisions during the optimization process. It is particularly important at the site level to involve stakeholders in collaborative decision-making. Effective stakeholder participation can promote a more accurate understanding of the relative risks of various technologies and remediation options. Participants gain a greater understanding of the regulatory requirements and processes, as well as a greater understanding of the technologies and/or remediation techniques, and are thus more likely to accept changes to the original remedial design.

The success of engagement programs depends on effective planning and outreach to build a working relationship between stakeholders and those conducting and overseeing remediation. By reaching out and responding to stakeholders not only when required by law, but throughout the process, regulators and responsible parties can build trust with stakeholders. Finally, including stakeholders in site decisions makes them partners in a process that protects them, their families, their property, and their communities.

Where there is significant community interest, environmental decision makers may find it useful to go beyond a one-time or occasional community meeting and create a project-specific community advisory board with representatives from each segment of the community. Such boards have improved community relations at numerous DOE, DOD, and private sites across the country. Community advisory boards and/or restoration advisory boards often provide remedial project decision makers with “one-stop shopping” for community input. Relying on community advisory boards or restoration advisory boards can help work out differences among various community members, avoiding any guessing or assuming which community interest represents the public.

The following steps outline an approach for effective stakeholder engagement.

6.4.1 Plan for Stakeholder Engagement

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Stakeholder engagement should not be an afterthought, but rather integrated into project staffing, budgets, and timetables from the beginning of the project. Project managers and their technical and legal teams should communicate with the public early on, and community involvement specialists—for organizations that have them—should be included in internal technical meetings so they are able to provide timely, accurate information to the public.

Project budgets should also include funding for stakeholder engagement. Effective programs recognize that funding for community relations, advisory boards, and independent technical assistance is an investment that pays off in better decisions and smoother progress, as well as public recognition of the work of those responsible for cleanup. Experience has shown that when regulators and responsible parties listen to communities near contaminated sites, the communities are empowered and are more likely to offer constructive guidance.

At large sites, some agencies routinely develop community involvement plans by interviewing community leaders to find out who is concerned about the site and why. This approach is also useful at sites with little history of stakeholder engagement, and is a good way to identify segments of the community that, for cultural or geographic reasons, have not participated in public events. For example, a community involvement plan might identify areas where residents have limited English-language capability and include translation needs in the project plan.

State and federal officials, as well as private responsible parties, should familiarize themselves with the multiple local governments, authorities, and relevant organizations that may have jurisdiction or control over a site. Many sites are bounded by multiple cities and may be served by counties and special districts. One good practice is to plan to attend city council meetings dealing with the reuse of contaminated sites to answer questions about the suitability of sites for reuse. Few local governments have the technical expertise to answer such questions on their own.

Plans for outreach and community involvement should also identify environmental justice communities potentially affected by the site. Underserved communities often feel excluded from or mistrustful of government programs, and may lack the technical background to feel comfortable taking part in discussions of technical issues. These communities should be brought into discussions of the fundamental issues facing cleanup programs, and planning should include efforts such as outreach, explanatory materials, and fact sheets in the communities’ primary languages.

6.4.2 Engage the Stakeholder Community Through Outreach

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Agencies sometimes prematurely conclude that there is minimal stakeholder interest at a site because of low attendance at official public meetings or open houses. Often, however, community outreach is needed to raise awareness about site issues. If people do not attend regulator-sponsored events, then regulators can arrange to present at neighborhood association or parents’ association meetings. In fact, outreach may prove helpful even if regulator meetings are well attended. Another approach is to partner with trusted community organizations to set up meetings.

In New Jersey and other states, regulations require public notice at various stages of a project and may include signage, letters, and newspaper notifications to property owners and tenants within specified distances of a site or plume, as well as notifications to the local town clerk, planning board, and health department. The responsible party is required to respond to media and public requests and to conduct public meetings, if appropriate.

6.4.3 Build Trust Through Communication

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Community acceptance of proposed remedies and cleanup standards often depends on whether the stakeholders trust the other parties involved. The first step in trust building is for regulators and responsible parties to inform the public that the site contamination affects their community, early and often. Usually one press release is not enough; people may miss a story and new arrivals often have no easy way to catch up on old news. Furthermore, regulators or responsible parties build trust when they announce how they are addressing a problem, rather than having news media expose the problem.

Project personnel should familiarize themselves with the various communication media, including bloggers, Facebook, Twitter, and Instagram, that can communicate with community and tribal stakeholders interested in their sites. Most people get their information about contaminated sites and cleanup from these media, not directly from the programs. In some cases, experienced reporters have, over time, developed a wealth of site knowledge, but usually reporters and broadcast news producers spend less than a day on each story. Some reporters embellish the negative aspects of a remediation project to attract headlines. Many reporters may miss the technical nuances, but are more likely to report accurately and constructively if regulators, responsible parties, and the stakeholders’ technical consultants take the time to explain site activities.

6.4.4 Build Trust by Clearly Explaining Technical Concepts

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For public meetings, regulators and responsible parties should understand the general level of technical background in the host communities. Some communities include engineers and scientists who understand scientific notation, are used to reading technical reports, and know how to address quantitative uncertainty, but most do not. Even those communities with strong general technical knowledge may not know much about hydrogeology, geochemistry, and the other fields that contribute to in situ remediation projects.

Presenters should limit the use of acronyms and be prepared to explain references to regulatory programs and responsibilities. Stakeholders often do not distinguish among government agencies, and few understand how agencies are organized. Consequently, the public may not understand lines of decision-making authority, particularly where the parties themselves do not agree.

Technical documents should be easily accessible and offered in printed form and, if possible, searchable standard electronic formats. Many sites have dedicated websites, which stakeholders can visit to download current documents, as well as earlier site documents referenced in current ones. These websites should contain links to documents for nearby sites and agency guidance documents as well. Some states maintain statewide databases where outside experts can easily find pertinent documents on behalf of local stakeholders. Because regulatory agency staff can fall behind in posting documents, sometimes stakeholders may need to request website updates. To build trust, new information should be posted in a timely manner.

6.4.5 Include Stakeholders in Decision-Making

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Stakeholders are partners in the decision-making process. As such, most stakeholders seek the opportunity to review draft documents while there is still time to change them. They object to the “decide-announce-defend” approach, in which regulators and the regulated negotiate for months to produce a draft document, and then feel obligated to defend the document against changes. It is harder for stakeholders to participate effectively when the other parties have already reached agreement. A better course of action is to engage stakeholders while work plans and reports are still being developed. Some project managers find it helpful to broach remedial concepts informally, giving stakeholders a chance to weigh in on an idea before it is included in a draft document.

6.4.6 Keep Stakeholders Informed of Progress and Results

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After optimization recommendation implementation, the stakeholders should be advised of the results of the process. The process should produce measurable results. The minimum measurable results that should be recorded are changes in protectiveness and changes in the remediation project’s time line and projected costs.

6.5 Communications

Effective communications with stakeholders can be achieved through knowledge and use of communication principles and skills. Stakeholder communication should not be considered public speaking, “spinning,” or embellishing messages. It requires being open, honest, genuine, and sincere and applying verbal and nonverbal skills in a variety of situations. It also requires an ongoing commitment to practice and preparation. Multiple benefits can be achieved using risk communication principles:

- improved relationships with stakeholders, which can result in increased/maintained trust
- efficient implementation of processes because of buy-in by stakeholders
- improved public perception
- fewer legal challenges when public involvement requirements have been satisfied
- less antagonistic experience with the media

6.5.1 Stakeholder Impacts

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Identify stakeholders who could impact the project favorably, neutrally, or unfavorably. Some stakeholders will oppose the project, regardless of efforts to include them in the process. Some stakeholders provide support from the start, recognizing the advantages of the remediation and the benefits of optimization. Most stakeholders are generally open to more information and finding common ground.

Develop a communication strategy that addresses all stakeholder motivations so that the relationship with supporters is maintained and the open-minded supporters receive the information they need to understand the process. An effective communication strategy should also show good faith to the stakeholders who have negatively prejudged the situation. Provide information, listen to their concerns, and invite them to the meetings. Demonstrate willingness for discussion.

6.5.2 Third-Party Supporters

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A third-party supporter is a stakeholder whom the majority of stakeholders see as trusted and knowledgeable. In tribal communities these can be elders and in many cases students. Third-party supporters can provide formal or informal support, including background or suggestions on approaches.

Local government officials, health departments, academia, and regulators can also be effective third-party supporters as respected figures with extensive experience with the community. Third-party supporters often are good sources for identifying additional supporters.

6.5.3 Proactive Approach

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Do not wait for stakeholders to learn about problems through other sources. Be proactive:

- Provide all the relevant information.
- Discuss the unknown factors.
- Update stakeholders as information becomes available.
- Communicate with stakeholders early and on a regular basis.

Being proactive is critical for successful communications with stakeholders. The longer an organization takes to provide information, the more difficult it is to overcome the perceptions associated with less than ideal results, the need for significant optimization, or remedy failures.

6.5.4 Training

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Ensure that all communicators are properly trained. Representatives should understand the technical and political aspects of a project and be prepared to address stakeholder concerns. Representative should not provide answers to questions unless they are sure of the facts. Most stakeholders will respect the representative who follows up to answer a question after the facts have been gathered.

6.5.5 Media

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Be prepared for your message to be totally misconstrued. Designate one official point of contact. This makes fixing errors so much easier. Build professional relationships with the media, if possible. Be aware that in these days of social media, any stakeholder could post information that may or may not be correct.

Issue fact sheets, statements, and notifications that are clear, concise, and understandable. Avoid technical jargon that could be misinterpreted as attempts to mask or cover up problems.

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Appendix A: Amendments and Other Additives

The following Fact Sheets discuss the Amendment and four topics related to it:

- Limitations
- Other Considerations
- Health and Safety
- Additional Links and Information

It is important to recognize that many amendments blur the lines between biotic and abiotic applications. Amendments are grouped under biotic and abiotic amendments in Sections A1 and A2, respectively, below based upon what we believe are the primary applications, but recognize that many amendments may fit into more than one category considered in multiple sections. Other additives, such as nutrients, pH modifiers, and methane inhibitors, are summarized in Section A3. Care should be taken to evaluate the likelihood of effective distribution of the amendment within the desired treatment zone, and of the effective microbial use of the amendment for beneficial transformation of the contaminant to meet the treatment goals. Care should also be taken to avoid adverse effects on the compliance monitoring wells. The current state of the practice often allows practitioners to be successful with any of these amendments given proper evaluation, planning, and application. Details of typical delivery methods are discussed in Amendment Delivery Optimization Section 3.6.

A1 Common Biotic Amendments

This section describes biotic amendments that are used to enhance biological degradation processes. This includes products designed to stimulate aerobic or anaerobic metabolic processes, and also cometabolic biological processes. Collectively, these three categories are intended to create optimal conditions for naturally occurring bacteria. The bacteria may use a variety of electron acceptors (oxygen, nitrate, sulfate, manganese, iron, carbon dioxide, yielding methane and chlorinated solvents). Growth of bacteria is favored at neutral pH, moderate temperatures, and the presence of inorganic nutrients such as nitrogen, phosphorus, and potassium. In addition, specialized bacteria can be added in a process called bioaugmentation, which is discussed in Section A1.4.

A1.1 Aerobic Bioremediation

In the presence of aerobic conditions and appropriate nutrients, microorganisms can convert many organic contaminants to carbon dioxide, water, and microbial cell mass. Many organisms are capable of degrading hydrocarbons using oxygen as the electron acceptor and the hydrocarbons as carbon and energy sources. Aerobic metabolism is more commonly employed and can be effective for hydrocarbons and other organic compounds such as petroleum hydrocarbons and some fuel oxygenates (for example, methyl tertiary-butyl ether [MTBE]). Aerobic bioremediation technologies may also change the ionic form of metals, though the permanence of these changes will depend on site-specific conditions. If a site contains mixed metal and organic wastes, it is necessary to consider whether the oxidized forms of the metal species (such as arsenic) will be environmentally acceptable (USEPA 2006b).

Aerobic oxidation can occur naturally under proper conditions, but oxygen, which is often considered to be the primary growth-limiting factor for hydrocarbon-degrading bacteria, is normally depleted in zones that have been contaminated with hydrocarbons. Common amendments used for aerobic bioremediation are air, pure oxygen, hydrogen peroxide, ozone, and commercial oxygen-releasing compounds such as magnesium peroxide, calcium peroxide, and calcium oxy-hydroxide. More information about the common amendments used for aerobic bioremediation is available in Table 3-2. Enhanced aerobic bioremediation technologies focus in part on increasing oxygen levels and can potentially increase biodegradation by several orders of magnitude over naturally occurring, nonstimulated rates. Enhancements can be used to address contaminants in the unsaturated zone, the saturated zone, or both. The stoichiometric ratio of oxygen per hydrocarbon is about 3 moles O_2 per 1 mole of hydrocarbons. The success of aerobic bioremediation highly depends on the ability to deliver oxygen to the hydrocarbon-degrading microorganisms. The effectiveness of a bioremediation system is largely dictated by the balance between oxygen sources, the oxygen uptake, and the degree to which oxygen is transported through the subsurface (USEPA 2004).

Technologies to accelerate in situ aerobic bioremediation include biosparging, bioventing, and directly injecting oxygen-releasing substances. These technologies work by providing an additional supply of oxygen to the subsurface, which then becomes available to aerobic bacteria. Most enhanced aerobic bioremediation technologies primarily address contaminants that are dissolved in groundwater or that are adsorbed to soil particles in the saturated zone. Enhanced aerobic bioremediation technologies are typically used outside source areas (USEPA 2004). To enhance aerobic bioremediation, nutrients (nitrogen, phosphorus, magnesium, etc.) and pH buffers may be added to the groundwater. More detailed information about the additives (nutrients, pH buffer, etc.) can be found in Section A3.

Limitations

- Fouling or clogging of the aquifer may occur due to the precipitation of oxygenated metal species, particularly iron and manganese.
- Biofouling may also occur when bacteria attach to, grow on, and block the well screen, filter pack, or formation surrounding a nutrient delivery well. Nitrate- and perchlorate-reducing bacteria have been found to cause significant fouling of nutrient delivery systems.
- Certain metals may be mobilized in the subsurface. Care must be taken to protect receptors such as surface water from mobilized metals plumes.
- Strong sources, including NAPL, are generally not conducive to aerobic biodegradation.

Other Considerations

- Electron acceptors are required for aerobic reactions.
- Ambient subsurface conditions (intrinsic permeability, groundwater gradient, conductivity, etc.) should be studied to ensure that they are conducive to placement and distribution of amendments and the natural geochemistry (pH, dissolved oxygen, ORP, dissolved iron concentration, etc.) is appropriate for aerobic reaction.
- Certain amendments may have patent restrictions.
- Some restrictions may apply due to concentrations of constituents in the amendment—that is, salts, metals.

Health and Safety

- General drilling considerations are required.
- Precautions are required when dealing with oxygen tanks, etc.

Additional Information

More detailed description of common amendments used for aerobic bioremediation can be found in (ESTCP 2005a; ITRC 2008b; USEPA 2000).

A1.2 Cometabolic Aerobic and Anaerobic Bioremediation

Cometabolic bioremediation may be aerobic or anaerobic. In either form, the contaminant is degraded as the result of microbial metabolism of another compound. The biodegradation of the contaminant does not yield any energy or growth benefit for the microbe mediating the reaction (USEPA 2000). In aerobic cometabolic bioremediation, the contaminant is oxidized (loses an electron) by an enzyme or co-factor (a substance, other than the substrate, whose presence is essential for the activity of an enzyme) produced during microbial metabolism of another compound with oxygen. In anaerobic cometabolic bioremediation, the contaminant is reduced (gains an electron) by an enzyme or co-factor produced during microbial metabolism of another compound in an environment devoid of oxygen.

Cometabolic processes used for the bioremediation of COCs involve increasing the populations of organisms that generally exist and propagate by consumption of a primary substrate (for example, methane or propane) while producing enzymes that fortuitously degrade the COCs. Because the organisms obtain no benefit from the ancillary degradation of the COCs they can persist and thrive in the absence of the COCs. As an example; the bacteria *Pseudomonas methanica* (a methane-oxidizing, or “methanotrophic” organism) degrades its primary growth substrate, methane, by production of the enzyme methane monooxygenase, which will then degrade many COCs even though the bacteria obtain neither energy nor carbon from these ancillary degradation reactions.

Although both aerobic and anaerobic cometabolic biodegradation of COCs has been observed, most cometabolic remediation applications are aerobic. COCs that have been shown to be degraded cometabolically under aerobic conditions include TCE, cis-DCE, VC, TCA, chloroethane, chloroform, methylene chloride, MTBE, 1,4-dioxane, THF, TNT, RDX, atrazine, PAHs, and some pesticides. For example; the general aerobic cometabolic biodegradation pathway of trichloroethene (TCE) by methanotrophs is shown in Figure A1-1 below.

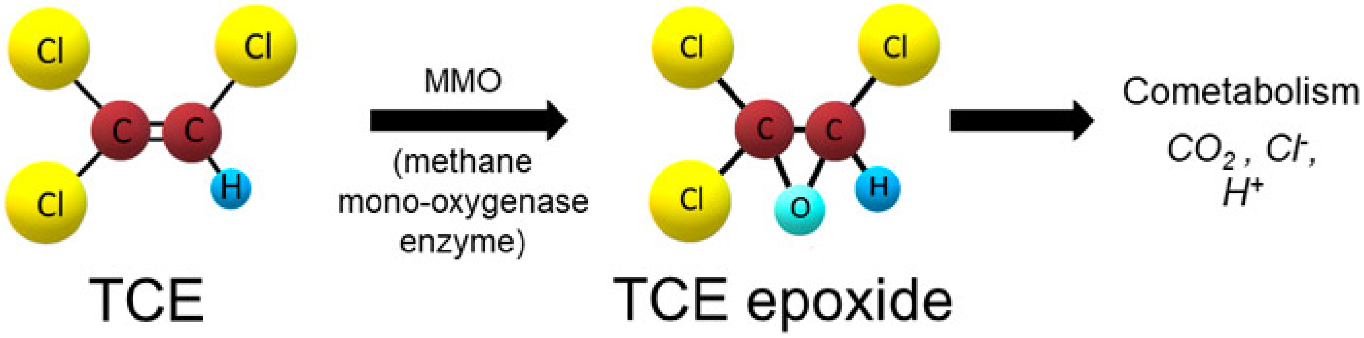

Figure A1-1. TCE oxidation pathways in methane-oxidizing bacteria.

The most common primary substrate amendments for aerobic cometabolic bioremediation include light alkanes, such as methane, propane, and butane, and alkenes, such as ethene and isobutene. If already present at the site in groundwater, bacteria can use other compounds such as toluene, phenol, methanol (Little 1988), and ammonia by as primary substrates.

Nutrients used to enhance cometabolic microbial growth include nitrogen, phosphorus, iron, magnesium, calcium, and trace elements (zinc, manganese, boron, cobalt, copper, nickel, and molybdenum). Oxygen is added to the subsurface to maintain sufficient aerobic conditions, and pH buffers such as sodium bicarbonate are added, as needed, to establish and sustain appropriate groundwater pH levels for the bacteria population. More detailed information about the additives (nutrients, pH buffer, etc.) can be found in Section A3. More detailed information about the bioaugmentation cultures can be found in Section A1.4.

Limitations

- Cometabolic bioremediation is limited by lists of contaminants that can be successfully cometabolized. For example, PCE and CT are not thought to be cometabolically biodegraded.
- Favorable subsurface geochemical conditions are required.
- Certain intermediates from the process may be toxic to microorganisms producing the enzymes.
- Under aerobic conditions, primary substrate and oxygen levels must be balanced to grow enough cells without oxygen depletion.

Other Considerations

- A contaminant itself may be used as a substrate in certain instances.
- Nutrients, oxygen, and pH buffers are added as needed to enhance microbial growth and maintain desirable subsurface conditions.
- Certain amendments may have patent restrictions or regulatory limitations based on ancillary components such as salts and metals.
- Bioaugmentation may be beneficial in certain cases.

Health and Safety

- Some gaseous substrates may be flammable.
- Hazards associated with substrates, nutrients, oxygen, and organisms must be taken into consideration.

Additional Information

- Bioremediation Review USEPA Cleanup Information (Last updated on February 7, 2019).
- (USEPA 2000). Engineered Approaches to In Situ Bioremediation of Chlorinated Solvents: Fundamentals and Field Applications.

A1.3 Anaerobic Biological Reduction

Under anaerobic conditions, certain types of microbes are capable of deriving energy by respiring organic compounds resulting in degradation of the organic compound via a reductive process. In general, anaerobic conditions are used to degrade highly halogenated contaminants though some petroleum hydrocarbons may also be biodegraded anaerobically. The halogenated compound, typically a chlorinated solvent, serves as the electron acceptor while hydrogen serves as the direct electron donor (USEPA 2000). Bacterial respiration results in replacement of a halogen (such as chlorine) with hydrogen, resulting in reduction of the parent compound. In bioremediation, the desired objective is to completely reduce contaminants to nonhazardous and environmentally acceptable products such as ethene, ethane, carbon dioxide, and chloride. Other bacteria can reduce inorganic compounds such as certain metals. Information regarding microorganisms is provided in Section A1.4.

Since the process of bioremediation was recognized in the early 1980s, efforts to enhance these biological processes have focused on development and distribution of organic substrates that can be effectively fermented to produce the hydrogen needed for dechlorination. Many types of electron donor amendments are used to promote reductive dechlorination (see "In Situ Bioremediation and Soil Vapor Extraction at the Former Beaches Laundry & Cleaners"). Examples include carbohydrates such as molasses, corn syrup and alcohols; carboxylic acids and triacylglycerols such as vegetable oils (that is, soybean, canola, etc.); and complex organics such as food processing byproducts (cheese whey) and natural organic matter (mulch) (see "In Situ Biological and Chemical Reduction of Hexavalent Chromium and Perchlorate"). Although electron donors can be categorized according to their chemistry, another way to characterize electron donors is according to their solubility. This allows a better understanding of their injectability. In general, these and other substrates can be divided into major categories based on the solubility properties of the amendment, for example, readily miscible and slowly soluble. The main differences in these categories are the injectability (Section 3.7) mechanisms by which the amendment can be effectively distributed within the treatment area (readily miscible) and the period that each amendment can be expected to remain reactive to promote the desired microbial processes (increases solubility). These characteristics are a function of the physical nature and properties of each amendment (ESTCP 2010a).

Limitations

- Anaerobic biological reduction is relatively slower than abiotic processes such as ZVI or ISCO.
- Degradation products may pose a greater risk than the parent product in some instances (for example, VC).
- Site-specific variables may inhibit establishment of appropriate conditions required for anaerobic remediation.
- Anaerobic conditions generated during remediation may affect other water quality characteristics of a site such as mobilization of iron and manganese or formation of methane.

Other Considerations

- Distribution of the amendment within the desired treatment zone and effective microbial use of the substrate should be evaluated.
- Solubility of the substrate should be considered to understand injectability and distribution in the subsurface.
- Certain amendments may have patent restrictions or regulatory limitations due to ancillary components of the amendments, such as salt and metals.
- Bioaugmentation may be necessary in some cases where there are low numbers of *Dehalococcoides* population and native microorganisms can't biodegrade all constituents (for example, VC).

Health and Safety

- Pressurized line hazards may be present.
- Proper storage and handling of amendments must be considered.
- This method may involve handling of pressurized and heated materials.
- Certain substrates may be considered hazardous due to flammability, corrosivity, etc.

Additional Information

- (ESTCP 2005a) Bioaugmentation for Remediation of Chlorinated Solvents: Technology Development, Status, and Research Needs.
- (USEPA 2000) Engineered Approaches to In Situ Bioremediation of Chlorinated Solvents: Fundamentals and Field Applications.
- (Government of Canada 2019) Bioaugmentation Fact Sheet
- (NAVFAC 2018) Advances in the State of the Practice for Enhanced In Situ Bioremediation 2018

A1.4 Bioaugmentation

Bioaugmentation is the process of adding microorganisms to the subsurface to enhance the existing microbial population and further promote the biodegradation of contaminants in the soil and/or groundwater. The selected microorganisms may be cultivated from existing populations present at a site (that is, indigenous) and grown in a laboratory, or from specially cultivated strains of bacteria having known capabilities to degrade specific contaminants (that is, nonindigenous). Bioaugmentation can be used to degrade contaminants in either aerobic or anaerobic conditions.

To effectively implement bioaugmentation, it is important to identify existing populations of indigenous microorganisms suitable for biodegradation and to evaluate:

- the functional genes of the organisms that tell us whether the contaminant can be degraded by that population
- their nutrient requirements
- the appropriate methods for stimulating degradation of target contaminants while minimizing competitive or undesirable microbial activities

The following is a list of the most common microorganisms typically used during anaerobic bioaugmentation:

Dehalococcoides is the most common microorganism genus used for anaerobic bioaugmentation. Only microorganisms belonging to the genus *Dehalococcoides* and *Dehalogenimonas* have demonstrated the capacity to dechlorinate dichloroethenes and vinyl chloride to ethene. *Dehalococcoides* also dechlorinate chlorobenzenes, polychlorinated dibenzodioxins, and PCBs. *Dehalococcoides* are microorganisms that require anaerobic conditions. Anaerobic biodegradation of target contaminants is often enhanced by an inoculation with *Dehalococcoides* or other appropriate microorganism-containing culture. Some strains of *Dehalococcoides* can metabolically degrade VC while others lack the enzymes for direct use of VC and may cometabolically biodegrade VC (this process is often slower and may require parent compounds). Therefore, it is important to know if the indigenous microbial population expresses the vcrA or TCA functional genes for VC reduction. Other VC reductase genes may occur but have not yet been identified.

Dehalobacter restrictus are bacteria capable of reductive dechlorination of chlorinated ethenes and chlorinated ethanes and fermentative dehalogenation of dichloromethane.

Sulfur-reducing bacteria use reduced or oxidized sulfur compounds in their energy transformations. For example, reduced sulfur compounds, such as sulfide and elemental sulfur, can be used by sulfur-reducing bacteria as electron donors or as energy and electron sources. In contrast, oxidized sulfur compounds, such as sulfate or hydrogen sulfide, can be used by sulfate-reducing bacteria as electron acceptors for the oxidation of organic compounds or matter. Sulfur-reducing bacteria also oxidize organic compounds or matter to obtain energy, but they use zero-valent sulfur as an electron acceptor.

Methanogens are microorganisms that produce methane as a metabolic byproduct in anoxic conditions. It is desirable and typical for *Dehalococcoides* to dominate the microbial population when promoting the dechlorination of dichloroethenes to ethene. However, in highly reductive environments, methanogens may dominate. Methane inhibitors may be introduced to manage and/or reduce methane concentrations during bioremediation. More detailed information regarding methane inhibitors can be found in Section A3.3 below.

Microbial consortia consist of two or more kinds of microorganisms acting symbiotically. Consortia provide a varied population of organisms to enhance the biodegradation of a suite of COCs and/or more complete biodegradation. In some cases, one group of microbes may produce co-factors such as vitamin B_{12} that dechlorinating bacteria need to complete the dechlorination reaction or to reduce intermediates that may interfere with further metabolism.

The effectiveness of enhanced aerobic bioremediation is a function of the presence of heterotrophic bacteria in the subsurface. If the background heterotrophic bacteria levels are higher than 1,000 colony forming units (CFU)/gram dry soil, enhanced aerobic bioremediation is generally effective. If the background heterotrophic bacteria levels are less than 1,000 CFU/gram dry soil enhanced aerobic bioremediation may be effective; however, further evaluation is needed to determine if toxic conditions are present (USEPA, 2017).

The chlorinated ethenes can degrade via cometabolic dechlorination (Fathepure 1987), although it is generally held that PCE is not amenable to aerobic cometabolic degradation, despite documentation of aerobic PCE cometabolism by *Pseudomonas putida OX1* by (Ryoo 2000). Other organisms, including *Pseudomonas putida* and *Methylosinus trichosporium OB3b*, degrade additional chlorinated compounds (for example, chloroethenes, chloroethanes, chloromethanes, and chloropropanes) via cometabolism (Heald 1994; Oldenhuis 1989). Unfortunately, despite the promise of the aerobic cometabolism approach, field implementation was found to be very challenging and was met with a series of incremental setbacks. First, introducing enough oxygen and cosubstrate proved to be difficult and/or expensive to implement (Steffan 1999). This led to the development of cultures using selected or genetically engineered microorganisms that would constitutively (that is, would not require induction by a metabolite) express these enzymes (Munakata-Marr 1996b). Although genetically engineered microorganisms have been developed, there are very few instances where they have been applied for bioremediation in field settings due to regulatory concerns and survival of the engineered microorganisms (Sayler 2000). However, adhesion of the introduced bacteria in the zone immediately surrounding the injection point limited the distribution of the microorganisms and the success of the bioremediation process for field-scale applications. To overcome this technical hurdle, both adhesion-deficient strains and ultramicrobacteria were developed (Cusack 1992; DeFlaun 1999) that possessed the desired degradation capabilities. However, after many years of field trials, aerobic cometabolism was determined to be too difficult for many to implement and sustain at most sites (relative to enhancing reductive dechlorination), and the approach has generally fallen out of favor for the remediation of chlorinated solvents. Cometabolic dechlorination may be suited for sites with very low concentrations of chlorinated solvents.

In some cases bioaugmentation with a known cometabolic degrader such as *Burkholderia cepacia G4*, *Methylosinus trichosporium OB3b*, and ENV425, or other propane oxidizers may be beneficial if the required bacteria population is not present or is found at very low numbers (Munakata-Marr 1996a) (Chang 1996).

Limitations

- Bioaugmentation culture will need electron acceptors or electron donors and neutral pH to survive.
- Presence of oxygen can significantly impact efficiency of strictly anaerobic microorganisms.
- Potential adverse impacts related to culture pathogenicity can occur.
- Microorganisms may not adapt to survive or there may be insufficient contaminant concentrations to support growth.
- Microorganisms may be consumed or outcompeted by other organisms already naturally present. The full microcosm must be understood.
- There is the possibility of deleterious metabolite(s) production.
- Bioaugmentation is not suitable for most inorganic contaminants.
- High contaminant concentrations may be toxic for microorganisms.
- Efficiency is affected by presence of metals.
- VC and/or methane concentrations may become vapor intrusion concerns.
- Biofouling may occur.

Other Considerations

- Identifying existing populations of indigenous microorganisms that are suitable for bioaugmentation at the site is pertinent.
- Nutrient requirements of microorganisms should be evaluated.
- Competitive or undesirable microbial activities should be minimized.
- Appropriate microbial culture should be identified based on target contaminants.
- Culture integrity should be maintained while producing sufficient quantity of organisms.
- Survival and performance of the added organisms should be monitored.
- Certain amendments may have patent restrictions.
- Explosive conditions may form due to methane production during reductive dechlorination.
- Microbial consortia can be used to target multiple COCs in certain cases.

Health and Safety

- Pressured line hazards can occur.
- Exposure to microorganisms may pose risks to human health.

Additional Information

- (USEPA 2000) Engineered Approaches to In Situ Bioremediation of Chlorinated Solvents: Fundamentals and Field Applications.
- (USEPA 2001) Use of Bioremediation at Superfund Sites EPA 542-R-01-019
- (Government of Canada 2019) Bioaugmentation Fact Sheet

A2 Abiotic Amendments

This section describes abiotic amendments that are used in abiotic degradation of contaminants. In some cases, the conditions created to encourage biological breakdown of contaminants will also be conducive to abiotic chemical transformation of the contaminants, which occurs without the help of organisms (Cwiertny and Scherer 2010). Added oxygen will oxidize many compounds without biological catalysis, and hydrolysis of organic contaminants can happen spontaneously. Zero-valent iron can be added to support anaerobic bioremediation by producing hydrogen as it oxidizes and to abiotically reduce contaminants.

A2.1 Chemical Oxidants

ISCO is the delivery of an oxidant to the subsurface to degrade or transform COCs. ISCO can be used for treating the vadose and saturated zones. ISCO is effective at treating a wide variety of contaminants at both the source area and within the aqueous plume (although it is more cost-effective per mole of contaminant at higher contaminant concentrations), and often produces decreased groundwater COC concentration results within weeks to months of the time of application.

Common oxidizing agents include catalyzed hydrogen peroxide (CHP, sometimes called modified Fenton's reagent), ozone, peroxone (the combination of ozone and hydrogen peroxide), activated and catalyzed persulfate, sodium percarbonate, and sodium or potassium permanganate. These oxidants are supplied in various forms. ISCO is amenable to treat groups of organic compounds (for example, BTEX, MTBE, CVOCs, SVOCs, carbon tetrachloride, select pesticides (for example, DDT, chlordane, lindane, etc.)), and some energetics (for example, dinitrotoluene or DNT, trinitrotoluene or TNT, and hexahydro-1,3,5-trinitro-1,3,5-triazine or RDX). ISCO is less effective on PAHs, PCBs, DCA, pesticides, chloroform, and metals that require reducing reactions and radicals. Some oxidants have narrow ranges of target compounds; for example, permanganate can attack only double bonds in compounds like PCE or TCE.

Limitations

- Certain amendments may cause exothermic reactions, leading to high temperature and pressure conditions.
- Amendments may cause high pH conditions problematic for biological growth.
- ISCO may not be economically feasible for low concentration large plumes.
- Metals impurities such as hexavalent chromium may be present in certain commercial-grade amendments and while in the reduced state can be reoxidized.
- Certain metals may be mobilized.
- Certain impurities or byproducts (for example, acetone, 2-butanone, etc.) may be introduced into groundwater as a result of the oxidation reactions.
- Byproducts from reactions can cause permeability reduction in the subsurface.
- Post-treatment contaminant rebound may occur.
- Certain amendments have a short life span, limiting migration in the subsurface.

Other Considerations

- Oxidant demand can depend on contaminant mass and distribution, presence of NAPL, geochemical conditions, SOD/NOD of treatment zone, and presence of oxidant scavengers.
- Specialized delivery systems may be required.
- Groundwater quality impacts from byproducts may trigger monitoring requirements.
- Certain amendments may have patent restrictions or regulatory restrictions due to ancillary components of the amendment, such as salts and metals.
- VOCs may volatilize during exothermic reactions.

Health and Safety

- Exothermic reactions could pose an explosive hazard.
- Health hazards may occur due to fugitive gas and dust emissions.
- Spills and releases onto combustible materials can cause fires.
- Pressurized line hazards may occur.
- Health and safety hazards related to handling of amendments should be considered.
- Oxidants and other amendments/activators should be stored with compatible chemicals, and material compatibility should be considered for the injection system components to avoid potential adverse reactions, failure of seals, etc.

- Consider applicable federal, state, and local regulations (for example, DOT, fire department) for transportation and on-site storage requirements.

Additional Information

- (ITRC 2005) ITRC In Situ Chemical Oxidation of Contaminated Soil and Groundwater
- (SERDP 2006a) In Situ Chemical Oxidation for Groundwater Remediation – Technology Practices Manual

A2.2 Chemical Reducing Compounds for Degradation Enhancement

In situ application of reducing compounds can degrade or chemically transform a variety of contaminants from toxic compounds to potentially nontoxic compounds. One example is provided in A Citizen's Guide to In Situ Chemical Reduction (USEPA 2012a). A second example is when ZVI comes in contact with TCE; the TCE is transformed to chloroacetylene and sometimes acetylene. Remediation using reducing compounds can decrease the concentrations of halogenated ethenes and ethanes, dinitrotoluene, and energetics, and transform some metals such as chromium (VI) and uranium (VI) and other metalloids to less toxic and less mobile forms. The most commonly used reductant is ZVI, which is used to remediate halogenated ethenes and ethanes, energetics, and some metals/metalloids (chromium (VI), arsenic, and uranium) (ITRC 2011c). Other reductants that are used to address metals include ferrous iron, sodium dithionite, sulfide salts (calcium polysulfide), and hydrogen sulfide (Dresel et al. 2011). The introduction of substrates to microbially produce reducing conditions favorable to microbial reduction of iron and sulfates also has been used to treat dissolved metal contamination (Waybrant et. al. 2002). Because of their higher surface areas, nano-ZVI particles are more reactive than larger ZVI particles. However, nano-ZVI particles can be consumed more rapidly by reaction with oxygen, nitrate, and sulfate, and won't persist in the environment as long as larger ZVI particles and generally are more expensive.

Limitations

- In situ application of reducing compounds is applicable for treatment of dissolved phase and soil phase if adequately distributed.
- ZVI as a reducing agent imposes a risk of hydraulic short-circuiting and aerobic iron corrosion. High concentrations of nitrate, sulfate, carbonate, or acidic conditions can corrode the ZVI or form precipitates coating the ZVI, thereby shortening the expected life span of the ZVI.

Other Considerations

- Metals are typically treated under alkaline conditions.
- Degradation of VOCs can occur via biotic or abiotic pathways.
- Combined reductants with sulfides and carbon substrates may be used.
- A multimechanism environment for reduction, adsorption, precipitation, and sequestration of heavy metals is currently being considered.
- ZVI-based amendments and other zero-valent metals that can be used as reducing agents are currently being studied.
- Influence of ZVI in the subsurface can lead to hydrogen production, which can promote growth of anaerobic microorganisms and enhance natural reductive degradation.
- ZVI can be combined with biosubstrates and bioaugmentation.

Health and Safety

- Hazards related to handling of the reducing agents must be considered.
- Depending on emplacement technique, pressurized line hazards or general heavy equipment hazards can occur.

Additional Information

- USEPA In Situ Chemical Reduction Overview Web Page

A2.3 Biogeochemical Transformations

The term "biogeochemical transformation" (BGT)" collectively describes the physical, chemical, and biological processes induced by reduced iron minerals in the subsurface, which transform contaminants into nontoxic daughter compounds. For instance, the reactive iron(II) sulfide degrades tetrachloroethylene (PCE) into ethene via the abiotic chemical reaction described below (NAVFAC 2015).

$$C_2Cl_4 + FeS + 4H_2O = C_2H_2 + Fe^{+3} + SO_4^{-2} + 4Cl^- + 6H^+$$

Other final degradation products including acetylene, ethene, and ethane can be formed from the reaction of PCE with ferrous sulfide. For this application, reduced iron minerals may be derived from naturally occurring geological formations or be formed by microbial activity under anaerobic conditions. Reduced iron minerals that have been exploited for remediation purposes include iron sulfides such as mackinawite (FeS), pyrite (FeS_2), magnetite (Fe_3O_4), and green rusts. Iron sulfides are often found naturally in anaerobic sediments such as wetlands and salt marsh environments. Green rusts are found naturally in soils and sediments in suboxic (low levels of oxygen and high levels of sulfur are present simultaneously) and anoxic (no oxygen) conditions. Iron sulfides, magnetite, and green rust have been studied the most because they are the most reactive. Among these three types of iron minerals, iron sulfides are the best understood.

For an in situ BGT application to be successful, there must be a balance between iron, sulfate, and electron donor in the system. Depending on the site conditions (determined through mineralogical studies, geochemical data, and/or microcosm studies), one or more of the three amendments may be required for the site. When using bioreactors and trench biowalls, solid amendments like mulch are typically emplaced. For injection approaches, liquid amendments are used. (For a more detailed description of the common amendments used for biogeochemical transformations, as well as targeted contaminants, please refer to (ESTCP 2005a).

Limitations

- Sulfate reduction requires neutral pH and abiotic transformation requires higher pH levels; therefore, careful monitoring of pH. is required.
- Iron fouling may occur.
- Less reactive FeS_2^- may form instead of FeS.
- Reactions may not be complete or may be slow.

Other Considerations

- Required subsurface conditions include high sulfate concentrations, high DOC, and presence of sufficient iron oxide minerals. These may be naturally present or introduced.
- Biogeochemical transformation is most efficient in anaerobic conditions and under low levels of naturally occurring biodegradation.
- Sufficient residence time for the amendment should be considered during design to allow for both sulfate reduction and abiotic transformation of contaminants.

Health and Safety

- Pressurized line hazards may occur.

Additional Information

- (NAVFAC 2015) Biogeochemical Transformation Handbook
- (Yongtian 2010) Identification and Characterization Methods for Reactive Minerals Responsible for Natural Attenuation of Chlorinated Organic Compounds in Ground Water

A2.4 Activated Carbon–Based Injectates

Carbon-based injectates (CBI) are in situ remediation amendments for contaminated soil, sediment, and groundwater. To differentiate these products from other organic carbon–based amendments frequently used for in situ remediation of chlorinated solvents, EPA refers to the technology as activated carbon–based technology. The activated carbon-based injectates (ACBI) are based on an adsorptive capacity of activated carbon (AC). The AC contains microscopic pores (micropores) that increase the surface area available for adsorption and chemical reactions. The AC adsorbs organic chemicals in the micropores through Van der Waals forces. Adsorption itself does not eliminate contaminants, but rather it limits migration. The primary mechanism for this media is typically sorption. Degradation of the compounds occurs by a secondary process (biotic or abiotic) on the media. Desorption is driven by the concentration gradients between the ACBI and the aquifer matrix. For contaminants not amenable to biotic or abiotic degradation, the sole treatment mechanism is adsorption of the contaminant.

The injectate is a mixture of powdered or pulverized AC, water, and additives such as electron acceptors, nutrients and microbes, or oxidants (Performance of Injected Powdered and Liquid Activated Carbon at a Petroleum Hydrocarbon Site). The AC adsorbs and concentrates the contaminants, which are then treated by additives within the mixture. Common ACBI amendments include gypsum to support sulfate-reduction breakdown of hydrocarbons or a soluble substrate to support anaerobic dechlorination or iron for abiotic breakdown of solvents.

A variety of secondary degradation mechanisms such as aerobic/anaerobic bioremediation and chemical reduction/oxidation can occur on the sorbed contaminants. The CBI amendments also provide a favorable environment for the natural processes, such as microbial degradations of contaminants.

Limitations

- Treatment effectiveness is limited by adsorptive capacity of the amendment, especially for contaminants not amenable to biotic or abiotic degradation.
- Contaminant flux into site may overwhelm rate of adsorption/degradation.
- Competitive adsorption may displace weakly sorbed compounds over time.

Other Considerations

- Long-term effectiveness data are currently lacking.
- Poor distribution of slurry-type amendments can occur in high or low permeability materials.
- Nutrients or amendments added to foster a biodegradation process will become depleted (some rather quickly), and there must be plans to monitor and periodically add more “food.”

Health and Safety

- Pressurized line hazards may occur.
- There is a potential for generation of fine particulates (carbon dust) and inhalation hazard during on-site slurry preparation or alternative emplacement techniques (for example, placement of dry carbon in excavation or trench).

Additional Information

- (USEPA 2018c) Remedial Technology Fact Sheet – Activated Carbon-Based Technology for In Situ Remediation

A2.5 Surfactants and Co-Solvents via Solvent Flushing

In some cases, surfactants are used to enhance solubility and bioavailability of contaminants from soil and sediments to improve treatment efficiency (West 1992; Rouse 1996; Perolo 2010). Solvent flushing involves injection of an alcohol/water solution (10–50 vol. %) to increase the NAPL solubility within the aqueous phase. Some alcohols may also result in a reduction of the NAPL/water interfacial tension and mobilize the NAPL. The aqueous solvent solution is injected into the subsurface so that it flows through the contaminated area. The solvent and dissolved contaminants are subsequently extracted and can be treated aboveground or sent off-site. As shown in Table 3-2, common surfactants used for in situ remediation applications include anionic surfactants, cationic surfactants, and electrolytes and co-solvents.

The primary mechanism for recovering NAPLs by using surfactants is either mobilization or solubilization. Surfactants can form micelles that can contain minute droplets of NAPL; hence the term “solubilization” is used to describe the apparent increase in NAPL solubility within the aqueous phase instead of the term “dissolution.” Although the two terms and mechanisms are different, the approach for using the solubilization mechanism is similar to that of dissolution, or pump and treat, where the recovery of NAPL is achieved by continuously injecting the surfactant formulation and producing solubilized NAPL. The degree of solubilization is typically two orders of magnitude higher than aqueous solubility, so a concomitant decrease in remediation time is achieved compared to standard groundwater extraction techniques. This approach has been called surfactant-enhanced aquifer remediation (SEAR) and differs from the surfactant flooding approach that relies upon mobilization as described below.

Surfactant formulations can also be used to reduce interfacial tension, which is the primary mechanism trapping NAPLs within the porous media. Such a formulation will allow the NAPL to become mobile and to be recovered from the subsurface. The surfactant used to solubilize vs. mobilize is often the same, as are the co-surfactants and other ingredients in the formulation. The behavior of the formulation, and hence whether it is used to solubilize or mobilize, is affected by parameters such as temperature, salinity, and other factors.

More background on surfactant phase behavior can be found in (Schechter. 1988; NFCSC 2002). Surfactants and solvents are useful to either increase apparent solubility or mobilize NAPLs. They are not used for dissolved groundwater plumes. NAPLs that have been candidates for surfactant or solvent action include TCE and PCE, creosote, gasoline, jet fuels, coal tar, and PCBs. In some cases; only laboratory scale feasibility studies were conducted, while in other cases a full-scale field implementation was completed.

Limitations

- There is a limited record of success for the in situ application of this technology.
- Surfactants may not recover dissolved components.
- Surfactants may not be compatible with most inorganic contaminants.
- Surfactants may not be suitable for soils rich in cationic materials or high organic content.
- This method may be less effective in low permeability and heterogeneous soils.
- Use of surfactant could increase dissolved phase contamination and NAPL plume size.
- This method requires pumping of groundwater to capture or hydraulically control NAPL.

Other Considerations

- Selection of surfactants should be made on a site-by-site basis because a wide range of surfactants is available.
- On-site or off-site treatment of recovered NAPL is required.
- Design should consider conditions to ensure capture of mobile NAPL.
- The high concentration of recovered NAPL can overwhelm existing on-site treatment systems.
- Cationic surfactants have not been used due to high surface adsorption.
- Some co-solvents, such as isopropanol, can result in byproducts. Separation of NAPL and surfactant to allow reuse of surfactant may make the process more economical. A treatment process to remove surfactant and co-solvent must be considered.
- Depending on the makeup of the amendment, there could be regulatory restrictions that must be met.

Health and Safety

- Solvents, surfactants, and co-surfactants are flammable.
- Relevant Safety Data Sheets should be consulted for proper PPE, handling, and storage requirements.

Additional Information

- (ITRC 2003) Technical and Regulatory Guidance for Surfactant / Cosolvent Flushing of DNAPL Source Zones
- (NFCSC 2002) Surfactant-Enhanced Aquifer Remediation (SEAR) Design Manual

A3 Other additives

To stimulate microbial growth and degradation of contaminants, supplemental amendments including those that directly support microbiological growth (C, N, P) and those that maintain or create favorable geochemistry (pH buffering, dissolved O_2) are used. Injection of small amounts of commercially available methane inhibitors is also recommended to retard the proliferation of methanogens to ensure the complete mitigation of any potential methane issue, as summarized below in A3.3.

A3.1 pH Buffers

At a field site, pH is influenced by a complex relationship between organisms, contaminant chemistry, and physical and chemical properties of the local subsurface environment. For example, in low-alkalinity systems, fermentation of complex substrates generates acids, and hydrochloric acid (HCl) is formed during anaerobic dechlorination. These processes may significantly decrease groundwater pH. Reducing groundwater pH to below 5 will likely inhibit microbial growth (for example, sulfate reducers, methanogens, and most dechlorinating microbes) (Maillacheruvu 1996). Normally, the natural buffering capacity of the aquifer matrix, as measured by alkalinity, is adequate to prevent the development of acidic groundwater pH; however, at some sites, pH buffer amendments may be required to maintain near-neutral pH in groundwater systems with insufficient natural buffering capacity. The maintenance of near-neutral groundwater pH is not only important for microbial growth, but also for secondary groundwater geochemistry.

For many acidic aquifers, pH buffering will be required to bring the pH into a range of 6–8, which is favorable for reductive dechlorination. Various pH adjustment agents have been used, including soluble materials such as sodium or potassium bicarbonate, sodium carbonate, sodium hydroxide, calcium hydroxide (slaked lime), or less soluble materials such as calcium carbonate, calcium oxide, magnesium oxide, magnesium hydroxide, dolomitic hydrated lime, and limestone. Bicarbonates have the lowest pH for saturated solutions of these buffers, but also have the least buffering capacity and the potential for carbon dioxide production. Calcium carbonate or limestone is practically insoluble, but has an equilibrium pH of 9.4. The other soluble reagents, including sodium hydroxide, sodium carbonate, and calcium hydroxide, have higher pH equilibrium levels and could therefore overshoot the desired pH range. The less soluble buffers are more difficult to deliver and generally have high equilibrium pHs (TerraSystems unpublised Report).

Common buffers include $CaCO_3$ (calcium carbonate), MgO (magnesium oxide), $Mg(OH)_2$ (magnesium hydroxide), $KHCO_3$ (potassium bicarbonate), $NaHCO_3$ (sodium bicarbonate), CaSx (calcium polysulfide), $FeSO_4$ (ferrous sulfate), $FeCl_3$ (ferric chloride), MgO (magnesium oxide), and CaO (calcium oxide).

A3.2 Nutrients

An aquifer normally contains sufficient amounts of nutrients for microbial growth. In engineered bioremediation; however, due to the presence of the contaminants or the addition of organic substrate, the nutritional demand imposed by rapid microbial growth may exceed the capacity of the aquifer system (Chamberlain 2003). In addition to a readily degradable carbon source, microorganisms also require nutrients such as N, P, and K for cellular metabolism and growth (Bamforth 2005). Commonly used nutrients include mineral salts (for example, KNO_3, $NaNO_3$, $Ca(NO_3)_2$, NH_4NO_3, $(NH_4)_2SO_4$, K_2HPO_4, $(NH_4)_2HPO_4$, $MgNH_4PO_4$,), anhydrous ammonia (NH_3), urea $(NH_2)_2CO$, and many commercial inorganic fertilizers. In practice, nitrogen and phosphorus requirements are often estimated by calculating a carbon to nitrogen to phosphorus ratio C:N:P close to 100:(10–5):1 (Atlas 1981; Atlas 1992). In practice, although most aquifers contain the necessary nutrients for microbial growth, nutrients are often added as an extra measure of assurance, and because they are generally inexpensive.

Dechlorinating bacteria such as *Dehalococcoides* do not produce vitamin B_{12}. Dechlorination efficiency can be increased by adding vitamin B_{12} to the aquifer. (He 2007; Harkness 2012) demonstrated the statistical value of nutrient addition in microcosm studies evaluating DNAPL TCE biodegradation.

A3.3 Methane Inhibitors

Methane concentrations may increase due to the proliferation of methane-producing bacteria, which occurs when high levels of carbon substrate such as emulsified vegetable oil are introduced into the subsurface. Methane can be metabolized by many microbes to carbon dioxide under aerobic conditions in the vadose zone. To ensure the complete mitigation of any potential methane issue, injection of small amounts of commercially available methane inhibitors is recommended to retard the proliferation of methanogens. “The methane inhibitor Provect-CH4 is a food-grade, natural source of Monacolin K (otherwise known as Lovastatin) that is used to prevent methane production by inhibiting the growth and proliferation of methanogenic Archaea. In environmental remediation applications, it can be used as a supplement to EISB and ISCR amendments, rendering them safer and more effective.” (Provectus 2014) It is supplied as a water-soluble powder that can be mixed on site and added in conjunction with the electron donor (NAVFAC 2018).

Appendix B. Commonly Encountered Issues with In situ Remediation

Commonly Encountered Issues Associated with Remedial Design Characterization – Section 2			
Lithology	**Contaminant**	**Challenges, Lessons Learned, and/or Best Practices**	**Discussion, Document Section, Links**
All		Reliance on MW data vs. a full understanding of contaminant mass distribution vs. lithology vs. permeability (K) available through higher resolution site characterization (HRSC) technology.	Continuous profiling tools such as MiHPT, MiHPT-CPT, LIF, LIF-CPT, LIF-CPT-MiHPT, MIP, MIP-CPT-MiHPT, etc., or continuous rock coring coupled with high density soil or rock sampling and physical and chemical analyses (ITRC 2015).
		Reliance on older CSMs that have not benefited from current investigation best practices, specifically higher resolution.	Fill data gaps with HRSC and update as needed based on injection performance monitoring.
		Unrealistic expectations without a full understanding of site-specific challenges, e.g., matrix back-diffusion, which can lead to contaminant concentration rebound after initial improvement in concentrations postinjection.	See Section 2. Knowledge of delivery and amendment limitations in achieving contact and adequate residence time with mass sorbed to the soil matrix.
		Uncharacterized contaminant mass due to site constraints, existing structures, utilities, roads, or other access limitations, which can recontaminate areas treated by injections (e.g., rebound).	Remedial design characterization and monitoring to evaluate mass flux from areas inaccessible for direct characterization; incorporate contaminant mass flux from these areas into amendment dosing and delivery design (ITRC 2010).
		Too much reliance placed on point permeability (K) measurement results and not enough on definition of transmissivity network, especially in fractured rock and in larger TTZs whether fractured rock or porous media.	Transmissivity network is directly related to mass flux concepts and can be better elucidated through tracer testing or aquifer pumping tests. Tracer testing conducted in drift mode is typically the most effective approach and, combined with continuous profiling or coring and selective groundwater sampling and analysis, can be highly effective in focusing remediation (ITRC 2010), (ITRC 2017a).

Commonly Encountered Issues Associated with Remedial Design Characterization - Section 2			
Lithology	**Contaminant**	**Challenges, Lessons Learned, and/or Best Practices**	**Discussion, Document Section, Links**
		Focusing narrowly on basic hydraulics, aqueous geochemistry, and contaminant chemistry and overlooking importance of biogeochemical features and processes.	Sites exhibiting organic and/or metal-metalloid COCs whose fates are susceptible to transport and fate processes influenced directly or indirectly by biogeochemical processes (e.g., redox, precipitation, sorption) may benefit from biogeochemical characterization and treatment considerations. Here, the sessile and planktonic microbes (often quite different populations), their biofilms, and neoformed (authigenic) amorphous and crystalline minerals can offer insight to treatment potential or unintended consequences. Designs can be enhanced, optimization options broadened.
Bedrock		The amount of contaminant mass sorbed into bedrock secondary porosity.	(ITRC 2017a)
Soil		Lack of understanding of contaminant mass sorbed onto finer grained soils.	Application of MiHPT, MiHPT-CPT coupled with high density soil sampling to determine extent and distribution of contaminant mass (ITRC 2015).
		Limitations of solvent extraction in quantifying mass sorbed into soil.	See Discrete fracture network approach for studying contamination in fractured rock
Groundwater		Variability of K and calculated seepage velocity in contaminated intervals is needed to estimate ROI delivery approaches and residence time within ROI.	Higher resolution slug testing, tracer testing, or pilot testing with monitoring to determine amendment distribution in effective pore space.
		Mischaracterization of mass flux to be targeted in a mass flux reduction strategy.	Higher resolution sampling to identify transmissive zones for injection based on defined targeted K values, contaminant mass, and heterogeneity within the TTZ.
	NAPL or DNAPL	Mischaracterization resulting in not identifying the presence of LNAPL or DNAPL that overwhelms efficacy of in situ treatment.	Evaluate vertical extent of TTZ for presence of LNAPL or DNAPL (ITRC 2015) (ITRC 2018).

Commonly Encountered Issues Associated with Amendment Delivery, Dose, and Design - Section 3			
Amendment Class	**Amendment Specifics**	**Challenges, Lessons Learned, and/or Best Practices**	**Discussion, Document Section, Links**
All		Reaction kinetics is consistent with time of contact.	See Appendix A for specific discussion of amendments, kinetics, and persistence of each amendment. Sections 3.3.2 and 3.5.1

Commonly Encountered Issues Associated with Amendment, Delivery and Dose Design- Section 3			
Amendment Class	**Amendment Specifics**	**Challenges, Lessons Learned, and/or Best Practices**	**Discussion, Document Section, Links**
		Sound design basis for ROI considering transportability within target intervals, e.g., liquids vs. solids, and seepage velocity.	See ROI, Section 3.3
		Lack of QA/QC evaluation of amendment and water to be used for both dilution of amendment and flushing purposes may introduce new contaminant(s) such as PFAS to the formation other than the targeted COC.	Check Safety Data Sheets of amendments before injecting and request detailed laboratory results of amendment showing the composition from the vendor. If potable water or hydrant water will be used for dilution and as chase water, request a lab analysis for PFAS or other contaminants or inorganic parameters (TDS, TSS, hardness, cations/anions, etc.) that might interfere with the chemical reactions. The details of PFAS sources, fates, etc., can be obtained from the ITRC PFAS Guidance document (in progress).
ISCO	**All**	Bench testing actual dosing vs. using default values to determine oxidant demand that is representative of full-scale implementation.	See Appendix A and Klozur® Persulfate Oxidant Demand
		General lack of basis for designing the number of injection events but rather using a rule of thumb.	See Appendix A and Klozur® Persulfate Oxidant Demand
		Bench testing is representative, as close as possible, to full-scale remediation design, e.g., water to soil ratios and taking into account the perfect mixing that occurs at the bench scale and not at full scale in regard to contaminant contact.	See Appendix A and Klozur® Persulfate Oxidant Demand
	CHP	Injection of peroxide, with or without activation in close proximity to petroleum free product, results in safety risks.	Hydrogen Peroxide (H2O2) Safety and Handling Guidelines
		Improper venting of injection system to avoid overpressurization and safety risks.	See Appendix A and Hydrogen Peroxide Safety and Handling
		Injection of CHP at too high a flow rate, resulting in excessive daylighting and lack of contact within target interval	See Appendix A – Conduct pilot test to define maximum flow rates and pressures and manifold to multiple locations if flow rates are too low to support project budget.
		Sequential vs. concurrent injection of hydrogen peroxide and iron activator result in inefficient contact for complete radical formation.	See Appendix A – USEPA- USEPA In situ Chemical Oxidation

Commonly Encountered Issues Associated with Amendment, Delivery and Dose Design- Section 3			
Amendment Class	**Amendment Specifics**	**Challenges, Lessons Learned, and/or Best Practices**	**Discussion, Document Section, Links**
		For chlorinated ethanes or methanes that require reducing radicals, bench testing is essential to determine percent reduction with this secondary treatment pathway from reducing superoxide radicals.	See Appendix A
	Persulfate	The background geochemistry, including TOD, is essential to identify the loading of base activator (NaOH). Persulfate can be used as direct oxidant or in an activation optimization process mode with multiple options for activation to generate radicals. If base activation is used, often with caustic NaOH, reactivity due to sulfate radical declines when pH falls below approximately pH 10. (Note: Some say 9.5, others 11). However, if following oxidation reaction residual pH is too high, this may adversely affect potential for further biodegradation without adjusting the pH.	See Chemical Oxidants Bench Testing (ITRC 2005) to determine buffering capacity of the soil Klozur® Persulfate Activation Guide
		Avoiding DPT injection of iron activated persulfate due to corrosion of carbon steel rods and tooling and comixing of iron and persulfate resulting in excessive heat generation.	See Section 3.3.2; and Chemical Oxidants Compatibility (ITRC 2005) Corrosion and Material Compatibility with Klozur® Persulfate and The Safe Use of Klozur® Persulfate Activators and ReMox® ISCO Reagent Material Compatibility Technical Brief and ReMox® Liquid Material Recommendations and Compatibility Technical Brief
		Avoiding overdosing caustic activated persulfate resulting in solids precipitation that could plug wells and injection tools (certainly reduce porosity of the formation).	See Klozur® Crystal Formation in Solutions of Klozur® SP and Klozur® Caustic
	Permanganate	Exceeding the solubility of potassium permanganate in water resulting in possible plugging (new) injection screen, filter pack, and formation.	See ReMox® ISCO Reagent Solubility in Distilled Water Technical Brief
		Storing and mixing of incompatible materials can lead to serious adverse effects. Care should be taken when the chemical oxidants are stored and mixed. Follow manufacturer's guidelines.	Burn Injury Caused by Mixing Incompatible Chemical with Sodium Permanganate

Commonly Encountered Issues Associated with Amendment, Delivery and Dose Design- Section 3			
Amendment Class	**Amendment Specifics**	**Challenges, Lessons Learned, and/or Best Practices**	**Discussion, Document Section, Links**
Anaerobic	**All**	Anaerobic biotreatment technologies are typically effective when geochemical conditions such as relatively lower redox (e.g., lower than –200 mv) are achieved. Depending on specific geochemical conditions, oxygen and one or more AEA (anandamide externally added) such as sulfate may need to be eliminated or greatly reduced before desirable treatment response is observed. Residual electron acceptor concentrations (e.g., sulfate and nitrate) may exceed water quality standards.	It is essential to collect background and baseline geochemical data, including electron acceptor demand, and to understand the existing biodegradation pathways before designing the loading for the amendment. Use a highly soluble amendment to stimulate sulfate reduction prior to dosing with a longer lasting amendment that will facilitate development of methanogenic conditions. (Note: It is not always desired to achieve methanogenic conditions.) See Appendix A1.3
	Soluble	Low persistence requires multiple injection events to overcome matrix back-diffusion.	Typically used to get anaerobic conditions started and then followed by nonsoluble. See Appendix A1.3
	Solids	Mulch, chitin, or other solids must be emplaced by trenching, soil mixing, or fracturing.	Must achieve adequate loading to promote degradation reaction within treatment zone, which depends on width of PRB trench and groundwater flow rate.
Aerobic	**All**		
	Solids	Estimating diffusive transport of slow-released oxygen source in finer grained soils to develop ROI.	Find the appropriate gas diffusion coefficient or conduct a treatability study (Allaire 2008). See Appendix A1.1
	Liquids	Short-lived release of oxygen from hydrogen peroxide requires multiple events.	Develop a good design basis for the amount of hydrogen peroxide needed considering its persistence and residence time within ROI, and plan for multiple injection events or continuous feed system if warranted. Consider different oxygen source. See Appendix A1.1

<table>
<tr><th colspan="4">Commonly Encountered Issues Associated with Amendment, Delivery and Dose Design- Section 3</th></tr>
<tr><th>Amendment Class</th><th>Amendment Specifics</th><th>Challenges, Lessons Learned, and/or Best Practices</th><th>Discussion, Document Section, Links</th></tr>
<tr><td></td><td>ZVI</td><td>Abiotic chemical reduction technologies of which ZVI and BiRD are two, typically express at least two reaction pathways: 1) beta elimination through acetylene series, and 2) hydrogenolysis through less chlorinated aliphatic DCE isomers and VC. Additionally, some fraction of PCE or TCE may concurrently transform via microbial hydrogenolysis. Often DCE and VC production is much less but still significant.</td><td>Evaluate potential for production of lower chlorinated compound and compare to regulatory goals. Often, effective understanding of chlorinated transformation product potential requires bench or pilot testing. Modifications might include sulfidization of the ZVI or bioaugmentation with <i>Dehalococcoides</i> spp. that (currently) are the only microbes known to promote direct and full dechlorination. See Appendix A1.1</td></tr>
<tr><td></td><td>Chemical</td><td>Calcium polysulfide solution should not be diluted below a 5% concentration, otherwise precipitation issues with sulfur develop as the pH drops during dilution.</td><td>Adding a caustic to dilution water helps maintain pH above precipitation levels.</td></tr>
<tr><td>Sorption and sequestration</td><td>Activated carbon and biochar-based injectates</td><td>Limited data to evaluate long-term effectiveness of sorption/sequestration technologies and potential for contaminant leaching from carbon over time.</td><td>Develop monitoring program to assess long-term effectiveness See Section 4.4 and transition and contingency planning See Section 4.6.</td></tr>
<tr><td></td><td></td><td>Injection of activated carbon may limit viability of subsequent treatment by other technologies due to changes in porosity, carbon content.</td><td>Design should be sufficient to achieve remediation objectives, or consider applicability of suitable combined remedies, e.g., enhanced bioremediation following carbon injection. See Section 3.4.1</td></tr>
<tr><td>Surfactant flushing</td><td>Surfactants, saponification agents, shear-thinning fluids (polymers), electrolytes</td><td>Surfactant flushing achieves contaminant mass recovery and can involve mobilization and solubilization, or only solubilization. However, surfactant flushing is most efficient when mass mobilization and recovery is the desired outcome. In this case, most mass would be recovered by mobilization and the balance by solubilization. A challenge is to correctly determine which mode to apply to site conditions and to provide sufficient recovery of mobilized and solubilized contaminants.</td><td>Bench testing and pilot testing are critical for surfactant selection and flushing and extraction design for full capture of mobile contaminants. See Section 3, Appendix A2.5, and Section 4.3, Implementation and Optimization Staircase (ITRC 2002a).</td></tr>
</table>

Commonly Encountered Issues Associated with Amendment, Delivery and Dose Design- Section 3			
Amendment Class	**Amendment Specifics**	**Challenges, Lessons Learned, and/or Best Practices**	**Discussion, Document Section, Links**
		Formation porosity reduction via mobile phase gelling or silt-clay migration and plugging by flocculation or straining is possible if the aqueous and sediment geochemistry is not adequately considered in surfactant system specification (e.g., surfactant, cosurfactant, electrolyte, etc.).	An important objective of bench-scale testing is to assess for adverse formation damage. One indicator that porosity reduction is occurring is the marked increase in back pressure during column flushing tests. It is noted that bench treatability testing for surfactant assessment efficacy and developing scalable design specifications must include a mix of batch and column flushing experiments. See Table 3-2
		Mobilization recovery is typically the most efficient means of LNAPL recovery if the hosting formation permeability/transmissivity is supportive (e.g., formation is porous media with average grain size of fine sand or larger and low clay and silt content). Shear-thinning fluids or polymers should be used in forced-gradient mode to help push the LNAPL, including previously immobile LNAPL at less than residual phase, out of the pores and toward the recovery well.	The bench treatability study should include tests for shear-thinning polymer selection and characterization, and polymer flushing stages should be included in column flushing tests. See Table 3-2
		One of the optimization opportunities with mobilization flushing is selection of a surfactant package that achieves low interfacial tension, e.g., three orders of magnitude or lower than interfacial tension between water and the oil phase in question.	Many commercial products or commodities with some surfactancy effect can produce a noticeable outcome in terms of NAPL mobilization or increased dissolved-phase concentration. Despite a noticeable outcome these products are relatively ineffective technically and economically for mobilization flushing and even enhanced solubilization mass removal. Well designed and operated bench studies can readily demonstrate the relative benefits of different products. See Table 3-2 Bench Testing: Objectives and Design Considerations

Commonly Encountered Issues Associated with Amendment, Delivery and Dose Design- Section 3			
Amendment Class	**Amendment Specifics**	**Challenges, Lessons Learned, and/or Best Practices**	**Discussion, Document Section, Links**
Enhanced solubilization flushing	Co-solvent, surfactant, clathrate	Agents designed for enhanced solubility functionality such as co-solvents (e.g., alcohols) and chlathrates (certain complex sugars) are sometimes specified or applied for NAPL mobilization flushing mass removal. These should be applied only to enhanced solubilization flushing operations. Surfactants are a special case where mass removal is possible via both enhanced solubilization and mobilization.	Bench testing is an important design component and necessary for optimization (ITRC 2018).

Commonly Encountered Issues Associated with Amendment Delivery – Section 3			
Amendment Class	**Amendment Specifics**	**Challenges, Lessons Learned, and/or Best Practices**	**Discussion, Document Section, Links**
All		Hydraulic design basis for ROI taking into account effective or mobile porosity and seepage velocity vs. persistence.	Ensure dosing and number of applications are consistent with projected advective distribution of amendments.
ISCO	**All**	Using vendor dosing calculator default values.	Suggest that you bracket the vendor estimates with science-based oxidant demand calculations and include a safety factor. (Note that chemical sellers are motivated to be conservative (include *safety* factors) so very much agree on independent work but the quantity may actually be less than proposed.) See Appendix A.2
		Issues with amendment safe handling concentrations.	Follow guidelines and recommendations from vendor. See Appendix A.2
		Consider solubilities of amendments in water.	If reagent exceeds aqueous solubility, not all of amendment will dissolve, resulting in precipitation of chemicals, which may reduce effective porosity of aquifer. Appendix A.2
	Catalyzed hydrogen peroxide	Using vendor dosing calculator default values vs. site specific values for peroxide concentration.	Determine dosing during bench scale testing with site soils. See Section 3.5
	Persulfate	Using vendor dosing calculator default values vs. site-specific values, e.g., buffering capacity, oxidant demand.	Determine dosing during bench-scale testing with site soils. See Section 3.5
	Permanganate	Using vendor dosing calculator default values vs. site-specific values, e.g., effective oxidant demand.	Determine dosing during bench-scale testing with site soils. See Section 3.5
BIO	**All**	Using vendor dosing calculator default values.	Make sure you bracket the vendor estimates with science-based calculations of electron donor/acceptor and include a safety factor.

Commonly Encountered Issues Associated with Amendment Delivery – Section 3			
Amendment Class	**Amendment Specifics**	**Challenges, Lessons Learned, and/or Best Practices**	**Discussion, Document Section, Links**
		Lack of degraders present to use the nutrients in a useful manner.	Evaluate use of biological/chemical testing (e.g., PetroTrap, CSIA). See Table 3-2
		Apparent lack of nutrients to sustain degradation.	Determine dosing during bench-scale testing with site soils. Verify during pilot testing. See Appendix A.1
Anaerobic	**All**	Overdosing resulting in creating methanogenic conditions.	Develop a design based on pilot testing and don't use rule of thumb concentrations. See Section 3.3.3
	Soluble	Substrate does not last long enough in subsurface to conduct performance monitoring or see reductions in target compounds.	Electron donor demand is higher than what can be provided with a soluble donor. Consider pilot testing a combination of soluble and less-soluble substrates. Another possibility is that the soluble substrate is not adequately distributed or the monitoring locations are not adequately placed. See Section 3.3.3
	Nonsoluble	Not adding or not adding enough buffering amendments to maintain pH in optimal range for CVOC biodegradation.	Determine during bench-scale testing with site soils. Verify during pilot testing and test pH and adjust as necessary when pH drop reduces remedy effectiveness. See Section 3.3.2
	Solids	Solid substrates, such as mulch or chitin, must be emplaced by trenching or soil mixing.	Consider adding mechanism to replenish PRB with a liquid substrate. See Appendix A1.3
	Gas	Hydrogen gas can serve as source of hydrogen for ERD.	Hydrogen gas is flammable and can be an explosive hazard. Consider how hydrogen gas will be mixed with groundwater and how often hydrogen gas cylinders must be replaced. See Appendix A1.2
Aerobic	**All**	Consider stoichiometry for release of oxygen compared to demand from NAPL, solid, and dissolved contaminant phases, reduced minerals, and NOD.	Determine oxygen release rates and distribution in bench scale or pilot testing. See to Appendix A1.2 Sections 3.3.2 and 3.3.3
	Solids	Consider stoichiometry for release of oxygen from solid oxygen-releasing compounds compared to demand from NAPL, solid, and dissolved hydrocarbon phases, reduced minerals, and NOD.	Many solid oxygen-releasing compounds are very alkaline and the elevated pH can impact microbial populations. See Appendix A.1.1, Section 3.5.2
	Liquids	Hydrogen peroxide is a source of oxygen as it decomposes. Too high of a dose of peroxide can be toxic to microbes or wasted if decomposition rate is too fast.	Start out with low hydrogen peroxide dose and increase over time. See Appendix A.1.1

Commonly Encountered Issues Associated with Amendment Delivery – Section 3			
Amendment Class	**Amendment Specifics**	**Challenges, Lessons Learned, and/or Best Practices**	**Discussion, Document Section, Links**
	Gas	Oxygen can be provided from air or purified oxygen and sparged into groundwater or introduced by bioventing.	Determine ROI for gas distribution. If sparging, consider pulsed injections to avoid preferential pathways. See Appendix A1
ISCR	**All**		
	ZVI	Using vendor dosing calculator default values versus site-specific values, ZVI weight percent to soil.	Determine dosing during bench-scale testing with site soils. See Section 3.5
		ZVI reducing equivalents may be funneled to water reduction up to ~99% and CAH (chlorinated aliphatic hydrocarbon) reduction as low as ~1%. The dose calculations portion of the design may not factor this in.	Bench or pilot testing can confirm ZVI efficiency for direct reduction versus H_2 (hydrogen) dissolved gas generation that might promote enhanced biotic reduction. Sulfidization of ZVI has been shown to effectively reverse the reducing equivalent flow (Semprini 1992).
	Liquids	Chemical reductants such as sodium dithionite, calcium polysulfide, or solutions of ferrous iron–containing compounds can provide ISCR reagents to subsurface or reduce existing iron in soil, and create reactive minerals such as ferrous sulfide.	Bench scale or pilot testing recommended to determine appropriate loading and confirm effectiveness in treating COCs. See Section 3.3.2 and 3.3.3
Sorption and sequestration	Activated carbon and biochar-based injectates	Dosing should be based on estimated contaminant mass across area and vertical profile of TTZ, including saturated zone soils.	Complete RDC soil sampling See Section 2.3
Surfactant flushing	Surfactants, saponification agents, shear-thinning fluids (polymers), electrolytes	Surfactant flushing can be applied to both LNAPL and DNAPL source zones. LNAPL sources are typically addressed through mobilization and DNAPL through enhanced potentially super-solubilization. It is desirable to mobilize LNAPL, and solubilization with increased contaminant dissolved phase concentrations will occur concurrently. Adverse impact will be minimal to nonexistent if the recovery well network is designed appropriately. Unlike LNAPL source zones, DNAPL source zones are often more complex and more difficult to fully characterize, and uncontrolled contaminant mass migration is more likely. Surfactant flushing is rarely applied to DNAPL.	Bench testing can generate data offering insights into the magnitude and extent of enhanced solubilization and desorption under either mobilization or enhanced solubilization approaches. The types of contaminants and concentrations, as well as other characteristics such as surfactant concentrations, pH, salinity, etc., are important for selecting effluent management approach and developing treatment specifications as appropriate. Field pilot testing is critical to effective assessment of magnitude and extent of contaminant mobilization. The pilot test should evaluate mass recovery approach and details including extraction well design for full capture.

Commonly Encountered Issues Associated with Amendment Delivery – Section 3			
Amendment Class	**Delivery and Amendment Specifics**	**Challenges, Lessons Learned, and/or Best Practices**	**Discussion, Document Section, Links**
All		Misapplying reagents not suitable for specific lithologies, e.g., solids in sands or liquids in clays.	Sands compact, rather than fracture, limiting the amount of amendment that can be emplaced. Injection velocities may need to be consistent with fluidization to obtain adequate distribution.
		Poor areal and vertical distribution.	Integrate delivery approach with amendment’s physical form and the target lithology.
		Delivery in shallow intervals results in daylighting.	Possible in all types of geology, sometimes due completely to anthropogenic features. Possible with coarse-grained soils at low flow rates and pressures.
		Delivery of liquids in soils that need to be fractured.	Typically liquids don’t have the residence time required to be effective in low pore volume applications required while fracturing.
		Determine whether injections will be advanced top-down or bottom-up and select appropriate injection tooling. Consider target lithology, injection pressures, and injectate type (e.g., aqueous solution or slurry).	For DPT injections a top-down approach generally results in more uniform distribution of reagent than a bottom-up approach. In a bottom-up approach, the borehole created by the rod and screen as they are raised can act as a conduit for downward migration of the reagent. Hence, a pyramid-shaped distribution of the amendment can result (NAVFAC 2013a). An exception would be in some flowing sands because the formation immediately collapses back into the void created by pulling up on the rods. Special injection tools can also help make bottom-up injections more successful in all lithologies. Injections using straddle packers, especially when sealing off directly onto the rock, are generally done bottom-up to increase the likelihood that the packer can be retrieved.
		Percent pore volume required for injection or emplacement for vadose zone remediation.	Vadose treatment requires injecting enough water to allow reactions to occur in the dissolved phase. Typically this would require 100% of pore volume to be displaced with diluted amendments. Liquids may drain from vadose zone.

Commonly Encountered Issues Associated with Amendment Delivery – Section 3			
Amendment Class	**Delivery and Amendment Specifics**	**Challenges, Lessons Learned, and/or Best Practices**	**Discussion, Document Section, Links**
		Groundwater displacement due to injection/emplacement of amendments that results in untreated contaminated groundwater leaving the site.	Develop a sound basis for ROI taking into consideration whether hydraulic control (e.g., extraction and recirculation) of groundwater used for dilution water to inject higher volumes is required for low seepage velocity sites. Also consider sequence of injections, specifically starting at the periphery and working in to mitigate migration risk.
	< fracture pressure injection	Not controlling and accurately recording injection pressures throughout the injection process.	Best practice would be an automated injection and injection performance data recording system.
	> fracture pressure injection	Unrealistic expectations on ROI.	Verification of amendment distribution during pilot testing. The design is not finished until the design is first implemented.
	> fracture pressure solids emplacement	Unrealistic expectations on ROI.	Verification of amendment distribution during pilot testing. The design is not finished until the design is first implemented.
	DPT delivery	Not factoring in compaction around the piping when controlling pressure and loss of pressure control as rods are added or removed.	Demonstrating compaction pressures during pilot testing and using inner hose direct push tooling to maintain constant injection pressure throughout the target interval and keeping the rods under pressure while advancing to the next injection depth. Monitoring of “breakout” pressure, and resultant drop (with increase in flow) is important to note during injection, and equipment must be sized to overcome initial injection resistance.
	Injection wells	Wells are not screened in the correct intervals that could have been optimized through high-resolution characterization.	Define target intervals for well screens with HRSC approaches before installation. Shorter screen intervals are often better but longer screen intervals can allow for more formation distribution and the possibility of acceptable performance.
ISCO	**All**		
	Catalyzed hydrogen peroxide	Increases in pressure when injecting rapidly reacting reagents, like H_2O_2, may signify gas generation and improper dosing/delivery. Safety risk by not venting all valves in contact with peroxide.	Vent all equipment in contact with hydrogen peroxide to prevent gas generation that has nowhere to escape and could cause a rupture of equipment and injury to operators.
		Low pH iron activation is incompatible with DPT drill pipe. Must inject through PVC.	pH < 2 will corrode pipe threads and they will not be retrievable.

Commonly Encountered Issues Associated with Amendment Delivery – Section 3			
Amendment Class	**Delivery and Amendment Specifics**	**Challenges, Lessons Learned, and/or Best Practices**	**Discussion, Document Section, Links**
	Persulfate	Iron activation incompatible with DPT drill pipe, must inject through PVC wells.	pH < 2 will corrode pipe threads and they will not be retrievable.
			Distribution can be verified by electrical conductivity logging, ORP, and pH readings during injections.
		Exceedance of auto decomposition concentrations.	> 30% concentration will react with itself and persulfate will be wasted.
	Permanganate	Mixing potassium permanganate above 2.5% without creating a slurry.	2.5% still requires good mixing and greater than 2.5% will require heating dilution water. Reconsider sodium permanganate.
			Distribution can be verified by soil coring and photo spectrometer to determine concentration.
Anaerobic	**All**	Pulsing of bioaugmentation cultures with an anaerobic blanket vs. mixing with anaerobic dilution water.	Ensure good in situ mixing of both amendments to obtain the same ROI.
		Poor distribution, resulting in discrete zones of concentrated mass of injectate, can lead to chemical and biological plugging of formation or at least low efficiency.	Design for undesirable concentration resulting from heterogeneous distribution with reduced injectate concentration or strength.
	Soluble	Distribution	Can be verified by changes in electrical conductivity in nested wells, or by temporary temperature changes. A tracer can be added to aid in visual determination, if site conditions do not include risk of daylighting.
	Nonsoluble	Distribution	Can be verified by changes in electrical conductivity in nested wells, or by temporary visual or temperature changes. A tracer can be added to aid in visual determination, if site conditions do not include risk of daylighting.
		Calculating an EVO (emulsified vegetable oil) loading only on hydrogen demand and not factoring in enough water to achieve ROI.	Factor in total volume of injectate, accounting for percent water in any vendor product, and the required volume of makeup water necessary to reach your design ROI. Make sure your calculations are checked by a third party.
	Solids	Poor mixing resulting in clogging and inconsistent delivery.	Define mixing equipment and time required to create homogenized slurry during preplanning or pilot testing event.
		Using emplacement tools not designed for solids.	Use pressure-activated emplacement tooling rather than screened tools. Anecdotal evidence suggests pressure-actuated injection points often fail to work.

Commonly Encountered Issues Associated with Amendment Delivery – Section 3

Amendment Class	**Delivery and Amendment Specifics**	**Challenges, Lessons Learned, and/or Best Practices**	**Discussion, Document Section, Links**
Aerobic			
	Solids	Emplacement at low flow rates resulting in not achieving ROI, unless ROI is just diffusion based.	Distribution requires exceeding fracture pressures at higher flow rates to create new pathways in order to approach design ROI.
	Liquids	Dilute hydrogen peroxide or dissolved oxygen in other forms can lead to biofouling of injection wells.	Consider pulsed injections of higher doses or incorporation of biofouling control reagent to prevent microbial growth on well screens.
ISCR	**All**		
	ZVI	Emplacement at low flow rates resulting in not achieving ROI.	Distribution requires exceeding fracture pressures and higher flow rates to create new pathways and achieve ROI.
		Emplacement of higher volumes than location can assimilate, leading to daylighting.	Verification of amendment distribution during pilot testing.
		Adequate mixing of ZVI and guar is required to prevent settling in tanks and injection hoses.	Educt guar into mixing tanks rather than applying by hand to avoid clumping of guar *fish eyes*. Replace guar with shear-thinning fluid or consider adding an emulsifier. Mixing equipment and injection pumps must be designed to work with slurries. The slurry must not be allowed to ‘settle’ anywhere within the injection equipment.
		Combining conflicting remedies (e.g., permanganate injection upgradient of ZVI barrier).	Manganese Dioxide can plug ZVI reaction sites.
		Distribution can be verified by soil coring and measuring magnetic responses.	Use of Magnetic Susceptibility to Map Amendment Distribution in the Subsurface, (Harkness).
	Liquids	Pulsing of calcium polysulfide with water flush may not result in uniform distribution within ROI.	Inject a diluted solution of at least a 5% concentration at the volumes required to achieve ROI based on advective flow.
		Using emplacement tools not designed for solids.	Use pressure-activated emplacement tooling rather than screened tools.
Sorption and sequestration	Activated carbon and biochar-based injectates	Injection of carbon as a slurry often requires high-pressure injection, which may exceed fracture pressures.	Verification of amendment distribution during injection via presence in wells, coring.

Commonly Encountered Issues Associated with Amendment Delivery – Section 3			
Amendment Class	**Delivery and Amendment Specifics**	**Challenges, Lessons Learned, and/or Best Practices**	**Discussion, Document Section, Links**
Surfactant flushing	Surfactants, saponification agents, shear-thinning fluids (polymers), electrolytes	Surfactant flushing can be applied to both LNAPL and DNAPL source zones. LNAPL sources are typically addressed through mobilization and DNAPL through enhanced, potentially super-solubilization. It is desirable to mobilize LNAPL, and solubilization with increased contaminant dissolved-phase concentrations will occur concurrently. Adverse impact will be minimal to nonexistent if the recovery well network is designed appropriately. Unlike LNAPL source zones, DNAPL source zones are often more complex and more difficult to fully characterize, and uncontrolled contaminant mass migration is more likely. Surfactant flushing is rarely applied to DNAPL.	Field pilot testing is critical to effective assessment of magnitude and extent of contaminant mobilization. The pilot test should evaluate mass recovery approach and details including extraction well design for full capture (ITRC 2002b).

Commonly Encountered Issues Associated with Field Implementation – Section 4			
Amendment Class	**Field Implementation-Technology, Amendment Specifics**	**Challenges, Lessons Learned, and/or Best Practices**	**Discussion, Document Section, Links**
All		Utilizing pumps that don't meet the specifications for effective distribution.	
		Utilizing mixing equipment that doesn't meet the specification for effective mixing required for effective distribution.	
		Defining downhole pressures based on pressure readings at the injection pump.	Have a good understanding of pressure losses throughout the injection system from the pump pressure gauge to the exit from the injection tool.
	< Fracture pressure injection	The inability of the injection system, as designed and operated, to maintain injection pressures below fracture pressures required for distribution.	Do not exceed fracture pressures to maintain controlled distribution.
	> Fracture pressure injection	The inability of the injection system, as designed and operated, to maintain injection pressure and flow rates above fracture pressures required for distribution.	Review pump curves of pressure vs. flow.

Commonly Encountered Issues Associated with Field Implementation – Section 4			
Amendment Class	**Field Implementation-Technology, Amendment Specifics**	**Challenges, Lessons Learned, and/or Best Practices**	**Discussion, Document Section, Links**
		Ensure all injection hose and pipe connection is pressure-rated for maximum pressures of the pump.	
	> Fracture pressure solids emplacement	The inability of the emplacement system, as designed and operated, to maintain injection pressures above fracture pressures required for distribution.	Review pump curves of pressure versus flow and size of solids it can pump.
		Ensure all emplacement hose and connections are pressure-rated for maximum pressures of the pump.	
	DPT delivery	Losing pressure control as rods are added or removed to achieve target depths.	Utilization of an *inner hose* system to maintain constant pressure.
		Ensure injection or emplacement tools are at target depth.	
		Ensure boring is straight to avoid daylighting around rods.	
		If injection rods are left in overnight, make sure they won't plug and require excess pressures and fracturing to restart injection.	
		Develop specific procedures on how to complete locations should daylighting or refusal prevent meeting dosing specifications.	
	Injection wells	Don't exceed pressure rate of well seal to avoid compromising well for future injection.	
		Monitor groundwater elevations at nearby wells to assess degree of mounding remains within design specifications and adjust injection rates and pressure as needed.	Consider automated injection systems that can be controlled based on groundwater elevations in nearby wells.
	Adequate distribution of amendments	Include adequate monitoring locations (wells or Geoprobe borings) and equipment in the design workplan to capture distribution. Downhole monitoring can be conducted using a variety of instruments to capture changes in physical and geochemical parameters during and immediately after injection.	See Section 4.4.1

Commonly Encountered Issues Associated with Field Implementation – Section 4			
Amendment Class	**Field Implementation-Technology, Amendment Specifics**	**Challenges, Lessons Learned, and/or Best Practices**	**Discussion, Document Section, Links**
	Performance monitoring	Postinjection monitoring data indicate an increase in concentrations following an initial decrease in contaminant concentrations, commonly referred to as “rebound.”	Re-evaluate CSM and potential causes of rebound, which may include back-diffusion from within the TTZ, recontamination of the TTZ from impacted areas outside of the ROI (see Section 2), inadequate dosing/persistence of reagents relative to contaminant mass (see Section 3).
ISCO	**All**	Maintaining injection pressures and flows during startup at multiple manifolded injection locations.	Ensure system design and operating procedures prevent fracturing of the formation. Consider automated systems as best practice.
		Health and safety plan, personal protective equipment (PPE), and associated Safety Data Sheets don’t address site-specific safety considerations.	Generic information is often not adequate to ensure safety. Focus on heat stress during hot weather.
		Ensure adequate protection of public when establishing work areas.	Public should never be in close proximity to injection locations that could spray them with oxidants and activators during equipment malfunctions.
		Injection while site is active for business.	Avoid this situation if adequate safety systems can’t be implemented, e.g., injection at active gas station.
	CHP	Daylighting events do not stop once flow is shut down. Exothermic energy input has been excessive and is driving pressure release for a period of time until pressure has declined enough.	Maintain injection rates, according to demonstrated specification to minimize daylighting.

Commonly Encountered Issues Associated with Field Implementation – Section 4			
Amendment Class	**Field Implementation- Technology, Amendment Specifics**	**Challenges, Lessons Learned, and/or Best Practices**	**Discussion, Document Section, Links**
		Installation of thermal couples to ensure groundwater temperature specifications are not exceeded.	Excess heat not only leads to daylighting but also decomposes the hydrogen peroxide quickly. Don't inject into NAPL zones. Cause and effect – excess H_2O_2 and catalysis lead to heat that leads to pressurization that leads to vaporization and concurrently leads to H_2O_2 decomposition, which leads to gas generation and to more pressurization and destabilization.
	Permanganate	Have adequate neutralization chemicals available for daylighting or spill events.	
BIO	**All**	No indications of change after amendment injection.	Verify groundwater flow direction, velocity, and lithology. Ensure that sampling locations and sampling depths are downgradient of the treatment area. Install temporary borings to check on distribution.
Anaerobic	**All**	Not achieving anoxic and pH specification for dilution water.	Note: pH may drop at least one order of magnitude (one pH unit) after mixing with amendment.
		Not achieving in situ redox conditions necessary for bioaugmentation culture to survive.	Check your site's ambient redox conditions, DO, pH, alkalinity, and dosing calculations to verify that the correct amendment and dosing are being used. Continue to monitor for change.
		An excess of methane is being generated in the surface as a result of amendment dosing.	Stop injection amendment and carefully monitor methane gas concentration in and around the wellheads. Provide supplemental mixing with air to reduce concentrations to below explosive limit. Research and implement safety precautions to prevent oxygen deprivation to potential receptors.
	Solids	Daylighting events do not stop once flow is shut down.	Maintain emplacement rates as those specified and demonstrated to minimize daylighting.
ISCR	**All**		

Commonly Encountered Issues Associated with Field Implementation – Section 4			
Amendment Class	**Field Implementation-Technology, Amendment Specifics**	**Challenges, Lessons Learned, and/or Best Practices**	**Discussion, Document Section, Links**
	ZVI	Plugging of injection tools due to inadequate mixing and suspension of ZVI.	Review mixing design and test during and verification of amendment suspension during pilot testing.
		Abrasion of emplacement tools from ZVI increasing emplacement port diameter.	Inspect tools after each location and replace as necessary. Inject port size directly impacts emplacement exit velocity, which impacts distribution.
		Adequate measurement of injection rates.	Consider mag flow meters vs. estimating tank level reduction over time.
	Liquids	Continuous monitoring of H_2S during calcium polysulfide injection.	H_2S generation occurs as calcium polysulfide is diluted with water.
Sorption and sequestration	Activated carbon and biochar-based injectates	Carbon presence in monitoring wells provides real-time evidence of amendment distribution during injection; however, carbon-impacted wells will need to be redeveloped to remove carbon from the well and filter pack, or replaced to ensure that groundwater samples provide contaminant concentration data representative of the aquifer for performance monitoring.	See Appendix A.2.4

Overall Challenges Associated with Section 5 Regulatory Perspectives & Section 6 Community and Tribal Stakeholder Considerations		
	Challenges, Lessons Learned, and/or Best Practices	**Discussion, Document Section, Links**
The traditional linear evaluation and decision-making process prevents implementation testing of an in situ treatment alternative.	Understanding that the successful application of in situ technologies is an inherently iterative process, that the regulatory process can allow for iterations within the traditional regulatory process, and that the early and close coordination of all stakeholders is essential, it is possible to optimize the regulatory process by building needed iterative assessments and adjustments into a project's decisions documents.	Section 5 and Section 6

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Appendix C. Characterization Parameters for In situ Treatment Remedies – Definitions and Descriptors for Table 2-2

NOTE 1–This table of “hover definitions” is to be used with Table 2-2. Each item in Table 2-2 has a corresponding definition here that is focused on the importance of the characteristic for in situ optimization.

NOTE 2–For additional technology-specific information, refer to Tables 4-2 through 4-6.

Physical Properties

Provenance and Mineralogy–Provenance and mineralogy of a rock or soil matrix are the properties of its physicochemical formation–geologic structure, chemical composition, distribution, and occurrence. They are the governing factors for the physical, flow, and geochemical properties, discussed in Table 2-2, that are necessary to understand and quantify in order to design an optimal in situ approach.

Stratigraphy–Stratigraphy describes the geologic layering in a formation. Formations with more layers (e.g., gravels, sands, silts) and complex “fingering” of high permeability units within low permeability media will require detailed characterization so that amendments can be emplaced properly.

Degree of Weathering of Geologic Formation–Generally, more weathered rock will more readily conduct water, and there will generally be less fracture flow and a higher degree of porous media flow. This can also be measured by the rock quality designation (RQD) described below.

Fracture Representative Aperture and Length–Fracture characteristics define the extent of fracture flow in a rock formation. Aperture is the representative fracture perpendicular width, and length is the representative length.

Fracture Connectivity/Rock Quality Designation (RQD)–Fracture characteristics define the extent of potential fracture flow in a rock formation. The connectivity of the fracture network determines the overall hydraulic conductivity of a rock formation; a highly connected fracture network will allow more flow. Rock quality designation (RQD) quantifies the degree of jointing or fracture in a rock mass by percentage, with >75% considered good quality hard rock, and <50% considered weathered.

Fracture Orientation–Fracture characteristics define the extent of fracture flow in a rock formation. In many formations the fractures are directionally oriented from the faulting that produced them. Orientation can influence the flow direction, even if the gradient is not aligned with the fractures.

Grain Size Distribution–Grain size is the diameter of individual particles of sediment, ranging from coarse (boulders, on the order of 10 inches) to colloidal (on the order of 10^{-8} to 10^{-5} inches). A formation’s ability to conduct groundwater will increase with grain size. Additionally, well-graded distributions will generally be less conductive than well-sorted distributions. If hydraulic testing has not been performed, grain size distribution can be used to estimate K via correlations provided in textbooks and literature.

Bulk Density–Bulk density of soil, measured in weight per volume, is used with the soil’s fraction of organic carbon to provide/calculate the carbon-water partitioning coefficient, which describes the affinity an organic chemical or contaminant will have for the soil matrix. It provides a measure of how much contaminant may be immobilized on the soil, and is important for *in situ* designs considering the incorporation of surfactants to release and treat such contamination.

Fraction of Organic Carbon–Fraction of organic carbon (F_{oc}), either unitless or in units of volume/weight, is used with the soil’s fraction of organic carbon to provide/calculate the carbon-water partitioning coefficient, which describes the affinity an organic chemical or contaminant will have for the soil matrix. It provides a measure of how much contaminant may be immobilized on the soil, and is important for in situ designs considering the incorporation of surfactants to release and treat such contamination.

Primary, Secondary, and Total Porosity–Primary porosity, measured as a fraction or percentage, is the volume of void space to total volume of soil or rock, and is considered a depositional feature. Secondary porosity is a post-depositional feature resulting from, for example, leaching of minerals or the generation of a fracture system. In remediation, a secondary porosity system can be developed using an engineered fracturing approach, which increases the available contact between amendments and the subsurface. Total porosity refers to the porosity resulting from both primary and secondary.

Transport Properties

Flow Regime–Flow regime refers to whether groundwater is confined, unconfined, or primarily governed by fracture flow. Groundwater occurrence significantly affects amendment emplacement design. For example, injection pressures are readily accommodated within an unconfined unit, but back pressure may limit distribution in a confined unit, which is already under pressure. Additionally, if a confined unit is mischaracterized as unconfined, the design may incorrectly call for amendment to be distributed within the vadose zone. Fracture flow presents unique challenges in fracture characterization and the general difficulty/inability to predictably distribute amendment.

Groundwater Occurrence and Variability–Groundwater occurrence is tied to a flow regime and can refer to groundwater depth, groundwater recharge from upgradient baseflow or precipitation, groundwater discharge boundaries such as lakes, rivers, and the ocean. These boundaries, in turn generally define the hydraulic gradient. For in situ design, deep groundwater can be a challenge for emplacement. In unconfined units, groundwater levels that fluctuate widely over the seasons or during droughts result in variability in the thickness of the saturated zone, and seasonal injection/reinjection events may be warranted. Finally, in heterogeneous or layered formations, groundwater may occur in separate hydrostratigraphic units, which must be identified during characterization and treated, possibly individually, during emplacement.

Hydraulic Conductivity–Hydraulic conductivity is a measurement of the rate at which a fluid (in our case, groundwater) will move through a permeable unit. Regardless of test methods (field or laboratory) or empirical data based on grain size, hydraulic conductivity is only an average representation of the overall unit’s ability to transmit groundwater. For robust in situ design, hydraulic conductivity must be taken in context and bolstered by knowledge of stratigraphy and groundwater occurrence, for example, so that permeable layers or stringers separated by less permeable layers will be appropriately targeted, and the unit will not be assumed to be homogeneous.

Degree of Heterogeneity–Heterogeneity refers to the variability in soil types within an aquifer (gravels, sands, silts, clays, bedrock/fractures). Heterogeneity is related to a unit’s provenance and conditions of formation, for example, alluvial units are more heterogeneous than fluvial units. Understanding and mapping the more permeable zones is a critical step in characterization, because these zones are more likely to be saturated with groundwater and contain contaminants. The less permeable units are more likely to have sorbed contaminants that will be slowly released over time via back-diffusion.

Anisotropic Orientation–Anisotropy refers to the directionality of physical aquifer properties. Layered units are generally isotropic, with continuity of properties and flow in the lateral direction, limited in the vertical direction by low permeability layers.

Effective Porosity–Effective porosity, a smaller number than total porosity, is the void space available for groundwater flow and injected amendment. “Unavailable” void space results from non-interconnected voids (e.g., as in some volcanic rock) or groundwater under surface tension (negative pressure) between soil grains, which prevents flow. For in situ design, effective porosity, not total porosity, should be used to estimate parameters such as seepage velocity and injected radius of influence. Further discussion of porosity and its effects on flow and transport are provided by ITRC (2015).

Velocity/Flux–Seepage velocity is calculated using Darcy’s Law ($v_s = Ki$), where i is the hydraulic gradient. Discharge velocity, or effective velocity, is the actual velocity of groundwater moving through soil pores ($v_e = Ki/n_e$), where n_e is the effective porosity. Flux is the velocity (seepage or discharge) through a vertical unit area of aquifer, which has the same units as velocity.

Aqueous Geochemistry

pH–The optimum pH range for aerobic or anaerobic biological activity is between 6 and 8, and certain amendments are prone to a reducing aquifer pH below the optimum range (see alkalinity). Some chemical oxidants (e.g., hydrogen peroxide/Fenton’s amendment) require low pH (i.e., 2.4) to be effective. During alkaline-activated persulfate oxidation and calcium or magnesium peroxide reactions, pH is expected to increase, typically above 10.

Temperature–For bioaugmentation, each microbial species has an optimal range of temperature for growth and survival; this optimal range should be obtained from the vendor and compared with the aquifer temperature during the selection process. Groundwater temperature can increase during the active injection period of many amendments. This depends on factors such as the difference in temperature between ambient air and subsurface, and whether the remediation process is exothermic. For example, during chemical oxidation reactions, temperature can increase notably and can be used, in part, to assess injection ROI.

Alkalinity–Alkalinity, measured in mg/L, refers to the capability of water to neutralize acid without changing the pH appreciably (also called buffering capacity). For acidic aquifers with low alkalinity, buffering may be required to neutralize the pH if a biological approach is selected. Even in a neutral aquifer, acids that may be generated from fermentation of organic substrates during biological activity could also lead to the need for buffering. Conversely, if magnesium or calcium peroxide is being added, the alkalinity of the groundwater can help determine the amount of a buffer or acid to add to mitigate the pH increasing to above the desired level (generally 8). Standard laboratory alkalinity tests can underestimate the base or acid demand.

Conductivity, Salinity, and Total Dissolved Solids (TDS)–Conductivity is a field measurement that can be converted to approximate salinity and TDS concentrations. Groundwater conductivity will typically increase during the active injection period of any amendment that introduces ions. In this way, increases in conductivity can be used, in part, to assess injection ROI. Elevated TDS can inhibit microbial activity in some cases. In the case of surfactant flushing, many surfactants will perform poorly unless the groundwater is at their optimal conductivity/salinity level; this needs to be screened prior to designing a flushing program.

Oxidation-Reduction Potential (ORP)–ORP in natural groundwater will range as high as 800 mV (highly oxidizing) to as low as -400 mV (highly reducing) and is a measure of oxidizing potential of a groundwater system. In contaminated groundwater, ORP often has decreased over time via natural degradation processes, especially if there is no groundwater recharge. Very generally, groundwater systems with high ORP may be candidates for chemical oxidation or aerobic biostimulation, while groundwater systems with low ORP may be candidates for anaerobic biostimulation or abiotic reduction. These remediation approaches will increase or decrease ORP during implementation, respectively. Note that pH and ORP values are inversely related, and dependent on the reference electrode used. ORP measurements alone, without integrating pH and metals concentrations into the analysis, can be misleading. ORP changes, not absolute ORP readings, are generally most instructive when examining the impacts of in situ remediation.

Dissolved Oxygen (DO)–Related to ORP, DO can range from close to zero to approximately 14 mg/L (at full saturation and cold water temperatures), and possibly higher in deeper wells. DO is a measure of the oxidizing potential of available oxygen. Groundwater is usually considered reducing if DO is less than 0.5 mg/L, and reasonably oxidizing at concentrations of 2 mg/L or more. In contaminated groundwater DO may typically have decreased over time via natural degradation processes, especially if groundwater recharge is slow. Very generally, groundwater systems with high DO may be candidates for chemical oxidation or aerobic biostimulation, while groundwater systems with low DO may be candidates for anaerobic biostimulation or abiotic reduction. These same remediation approaches will create an increase or a decrease in DO during implementation. For anaerobic bioremediation projects, higher doses or more frequent injection of electron donor can overcome an elevated DO. Dissolved oxygen is often difficult to measure in the field. If the ORP is negative, and there is evidence for anaerobic microbial activity (reduction of nitrate or sulfate, or production of methane), then elevated DO levels should be evaluated carefully. As with ORP, changing and controlling DO over a long time frame may be difficult and costly.

Nitrate (NO_3^-)–Nitrate can be naturally present in groundwater as a product of geologic formations and their naturally occurring minerals. It is also a widespread agricultural contaminant and may in fact be a target compound for in situ remediation. Natural or preremediation nitrate acts as a competitor for electrons during biological in situ reduction, and will typically react with carbon amendments more readily than typical target compounds such as chlorinated solvents. Nitrate concentrations as low as 1 mg/L can indicate competition and need to be taken into considered during amendment dosing.

Nitrite (NO_2^-)–Nitrite is the first product of nitrate reduction and its presence typically indicates a reducing groundwater environment. Nitrous oxide (NO) and nitrogen gas (N_2) are also produced during nitrate reduction. These compounds may be present at low concentrations or transitory. Oxygen will typically be reduced prior to nitrate; this is a generality, as this complicated process also depends on the microbial populations present and the relative concentrations of electron acceptors and electron donors in the groundwater.

Manganese (manganic, Mn^{4+})–Manganese is naturally present in many groundwaters as a product of geologic formations and their naturally occurring minerals or from sodium or potassium permanganate ISCO injections. Mn^{4+} acts as a competitor for electrons during in situ reduction, particularly at concentrations of approximately 50 mg/L or more. Conversely, during in situ oxidation, Mn^{4+} can be formed and mobilized from Mn^{2+}, inadvertently creating manganese plumes that can be of concern to regulators. When used to assess electron acceptor competition, total manganese should be measured by the laboratory.

Manganese (manganous, Mn^{2+})–Mn^{2+} is the product of Mn^{4+} reduction, and its presence typically indicates a reducing groundwater environment. Mn^{2+} is almost exclusively present in dissolved form in groundwater, and it should be analyzed in a filtered sample. For projects undergoing in situ oxidation, an Mn^{2+} baseline should be established to assess the potential for manganese mobilization, if this is a regulatory concern. Following electron donor injections, Mn^{2+} can increase.

Iron (ferric, Fe^{3+})–Iron is naturally present in many groundwaters as a product of geologic formations and their naturally occurring minerals. Fe^{3+} acts as a competitor for electrons during in situ reduction. When used to assess electron acceptor competition, total iron (which will almost always be present as Fe^{3+} and other oxidized forms) should be measured by the laboratory. When used to assess the oxidative-reductive environment, an additional dissolved Fe^{2+} (filtered sample) should be analyzed.

Iron (ferrous, Fe^{2+})–Fe^{2+} is the product of Fe^{3+} reduction, and its presence typically indicates a reducing groundwater environment. Fe^{2+} is almost exclusively present in dissolved form in groundwater, and it should be analyzed as a filtered sample. Iron will accept electrons with approximately the same competitiveness as many chlorinated solvents. Following electron donor injections, Fe^{2+} generally increases. In the presence of some oxidants (e.g., persulfate) where localized acidification following oxidant decomposition may occur, Fe^{2+} may also increase temporarily.

Sulfate (SO_4^{2-})–Sulfate is naturally present in many groundwaters as a product of geologic formations and their naturally occurring minerals and is often elevated in saline waters. It can also be a manufacturing or agricultural contaminant and a byproduct of persulfate used in some ISCO treatments. Sulfate needs to be carefully considered when selecting a remedial approach, as it can be beneficial and impeding, depending on the technology selected. Natural or preremediation sulfate at elevated concentrations can inhibit reductive processes such as reductive dechlorination, because sulfate, at elevated concentrations, is a powerful competitor for electrons. Typically, approximately 400 mg/L or greater sulfate at preremediation conditions can be a potential cause for concern (for reductive dechlorination) and special consideration for dosing. On the other hand, sulfate can react in situ with iron to form iron sulfides, which can provide long-term anaerobic chemical reduction. Sulfate reduction is yet another process, where sulfate is used as the primary electron acceptor, that can degrade specific contaminants (i.e., petroleum hydrocarbons).

Sulfite (SO_3^{2-}) and Sulfide (S^{2-})–These are the products of sulfate reduction, and their presence typically indicates a strongly reducing groundwater environment. Oxygen, nitrate, manganese, and iron will typically be reduced prior to sulfate. This is a generality, as this complicated process also depends on the microbial populations present and the relative concentrations of the electron acceptors in the groundwater. Sulfide can react in situ with ferrous iron to form ferrous sulfide precipitates and little free sulfide will be detected. Some aquifers, such as limestone or other fractured bedrocks, may have little bioavailable iron and sulfides, which may facilitate long-term anaerobic chemical reduction capacity. If hydrogen sulfide is formed, this can be toxic to microbes.

Chloride (Cl-)–As reductive dechlorination occurs chloride ions are released and the concentration of chloride may increase. However, natural and anthropogenic chloride may be present in groundwater at concentrations high enough that this change could be difficult to detect or attribute solely to remediation of the chlorinated solvents. In high chloride environments, such as landfills and areas subject to seawater intrusion, chloride can cause toxicity to microbes, typically at concentrations in the thousands of mg/L.

Chemical Oxygen Demand (COD)–COD in soil or water is the total measurement of all chemicals that can be oxidized. It is a measure of the total species, including the target contaminants, that will compete for an injected oxidant and is important in selection of oxidation as an appropriate approach, and dosing. It is important to include both soil and groundwater in COD testing, as both will be available to react with the injected oxidant. In addition to humic substances and dissolved organic matter, the presence of petroleum contaminants and reduced metals can contribute to the COD. In general, chlorinated solvents are in a more oxidized state and will not contribute appreciably to COD.

Soil Oxidant Demand (SOD)–SOD is the amount of a specific oxidant consumed by the soil. SOD tests are performed in the laboratory using site soil and the specific oxidant(s) under consideration for the site, and provide design data. In an SOD test, site groundwater is not used, and the site soil may or may not be from a contaminated portion of the site; therefore, SOD is a partial measure of Total Oxidant Demand (see TOD).

Total Oxidant Demand (TOD)–TOD is the amount of a specific oxidant consumed by all constituents (natural and contaminant) present in the soil and via the autodecomposition of the oxidant itself. Impacted groundwater may sometimes be used in the test. TOD tests are performed at varying oxidant concentrations using site matrix materials and the specific oxidant(s) under consideration to inform ISCO design. TOD may be the major component of chemical costs for a project.

Natural Oxidant Interaction (NOI)–NOI is a holistic term to describe the interactions among oxidant, oxidant dose, naturally occurring reductants and catalysts, multiple inorganic species in soil and groundwater, and the natural organic matter (NOM) and seeks to model the behavior of various oxidants under similar conditions by accounting for the concentration of the oxidant, catalyst, and NOM reactions. NOI is a comprehensive term, recognizing that the reaction kinetics and persistence of the available chemical oxidants vary greatly, sometimes leading to confused use of NOD/SOD/TOD.

Total Organic Carbon (TOC)–TOC provides an indication of the potential for biological activity/degradation to occur. TOC includes both naturally occurring organic carbon (such as humus) and organic carbon contamination, e.g., benzene. TOC values above approximately 50 mg/L indicate carbon levels that, if biologically available, could foster cometabolism. TOC may be depleted in areas where such cometabolism has already occurred. During the addition of a carbon source for biostimulation, TOC is expected to increase and can provide a measure of the injection ROI. Over time TOC will decline again to preremediation levels. This, combined with aquifer flow and transport information, can indicate when the substrate is depleted. TOC also provides a general indication of the amount of oxidant that will be needed, if a soil sample cannot be collected for testing.

Anions and Cations–These are the species comprising conductivity, salinity, and TDS. These species can become oxidized or reduced in areas undergoing in situ remediation. The most important anions and cations are discussed individually within Table 2-2. Like conductivity, anions and cations may be used to document preremediation baseline groundwater conditions and changes subsequent to the addition of a remediation injectate.

Arsenic (arsenite, As^{3+}, and arsenate, As^{5+})–Arsenic is naturally present in many soils and groundwaters as a product of geologic formations and their naturally occurring minerals. Arsenic has also been widely used as a pesticide for golf courses, orchards, wood treatment, and other uses. During in situ oxidation, arsenic can be mobilized, inadvertently creating an arsenic plume. The presence of arsenic both in soil and groundwater should be established prior to remediation of other compounds by oxidation, and laboratory testing can be used to assess the potential for transformation and mobilization. Many regulatory bodies require preremediation and postremediation testing for arsenic in groundwater. Arsenic concentrations may also increase after electron donor injections as arsenate is reduced to arsenite. Arsenic should be measured as an unfiltered sample. Amendments should also be assayed for arsenic by the batch, prior to use. Assessing arsenic presence and mobility should be combined with an evaluation of ferrous and ferric iron given the close geochemical interaction that occurs between the species.

Chromium (trivalent, Cr^{3+})–Trivalent chromium is naturally present in many soils and groundwaters as a product of geologic formations and their naturally occurring minerals. During in situ oxidation, hexavalent chromium (Cr^{6+}) acts as a competitive electron acceptor and trivalent chromium can be transformed into the more mobile and toxic hexavalent chromium (see Chromium, hexavalent), inadvertently creating a chromium plume. The presence of chromium in both soil and groundwater should be established prior to remediation of other compounds by oxidation, and laboratory testing can assess the potential for transformation to the hexavalent form. Amendments should also be assayed for chromium by the batch, prior to use.

Chromium (hexavalent, Cr^{6+})–Hexavalent chromium is the common oxidized form of trivalent chromium. Though naturally occurring in some locations worldwide, Cr^{6+} is of greatest concern as an anthropogenic compound, both as a byproduct of in situ oxidation and, importantly, as a contaminant source itself. Hexavalent chromium has had many applications in electroplating, wood treatment, etc. Indeed, in situ chemical reduction is often employed to remediate Cr^{6+} to its less mobile and less toxic Cr^{3+} form. Cr^{6+} is present almost exclusively in dissolved form in groundwater, and it should be analyzed as a filtered sample. (Note, however, that dissolved analyses may be acceptable for remediation design and monitoring, but in some states total metals may be required for regulatory site closure.) There are also specific colorimetric and ion chromatography methods for hexavalent chromium.

Other Heavy Metals (e.g., lead, copper, selenium)–Various metals may be naturally present in groundwater based on provenance and mineralogy. These should be assessed on a site-specific basis as part of in situ remediation planning. See Tables 4-2 through 4-6 for select discussion of some metals in relation to technology-specific applications.

Stable Isotope Probing–Stable isotope probing (SIP) tracks the environmental fate of a “labeled” contaminant of concern to assess whether biodegradation is occurring. The “label” serves as a tracer, which can be detected in the end products of biodegradation (e.g., new biomass or carbon dioxide). For a SIP study, test media (commercialized, for example, as Bio-Traps) are “baited” with a synthesized form of the contaminant containing ^{13}C as the label. Since ^{13C} is rare, carbon originating from labeled contaminant can be distinguished from ^{12}C from other sources. If biodegradation is occurring, the 13C label from the synthesized contaminant will be incorporated into microbial biomass and CO_2. SIP studies can be performed for any compound that microbes use as a carbon source, e.g. BTEX.

PLFA (phospholipid Fatty Acids)–PLFA are a main structural component of the outer membrane of all microbes. The presence and ratios of certain PLFAs aid in identifying broad groupings of microbe types (e.g., iron reducers, sulfate reducers, fermenters), that comprise a microbial community. Understanding can also be gained of the total biomass, functional groups, and relative health/activity before, in response to, and following an in situ remedy. PLFA is a useful tool to help identify whether biostimulation is an appropriate remedy for a site and whether bioaugmentation is needed. During remediation, the ongoing presence or increase in the biomass and changes to microbial community groups can be used to evaluate response to a remedy. PLFA cannot be used determine if bioaugmentation will be helpful for chlorinated solvent impacted sites, as the test does not detect dehalogenators within the microbial community.

qPCR (Quantitative Polymerase Chain Reaction–qPCR, commercialized in various forms is a molecular biological tool that quantifies the number of genes present in a sample. CENSUS can establish the presence of: Dehalococcoides and Dehalogenimonas, the only known microbes to fully dechlorinate PCE or TCE to ethene; Dehalobacter, which degrades chlorinated ethanes and methanes; Dehalogenimonas, which degrades chlorinated propanes; and other functional reductase genes such as the tceA, vcrA, and bvcA that demonstrate the metabolic potential to degrade TCE and VC. Sulfate reducing bacteria nitrate reducing bacteria and methanogens can also be identified. The presence of these genes at a chlorinated solvent impacted site can help identify whether biostimulation is an appropriate remedy for a site and whether bioaugmentation with a dechlorinating enrichment is needed. During remediation, the ongoing presence or increase in the concentration of these genes can be used to demonstrate performance. Quantarray can also identify aerobic microorganisms useful for remediation of petroleum hydrocarbons or which may compete with anaerobic microorganisms. These concepts and tests are discussed in detail in ITRC (2013a).

Degradation Potential

CSIA (Compound Specific Isotope Analysis)–Many elements of biological interest have two or more common stable isotopes, with the lighter isotopes present in much greater abundance than their heavier counterparts. For example, the abundance of the light isotope of carbon (^{12}C) is 98.89 percent and the abundance of the heavy isotope of carbon (^{13}C) is 1.11 %. Under conditions in which abiotic or biotic degradation of a compound is occurring, the parent compound gains a progressively higher content of heavy isotopes. This is because bonds between a heavier isotope and the atoms adjacent to it are stronger than the equivalent bonds of a lighter isotope. As a result, chemical or biologically mediated reactions of molecules that contain lighter isotopes occur more quickly than those that contain heavier isotopes. This process is called fractionation. Conversely, processes other than degradation that affect contaminant concentrations in groundwater, such as dilution, sorption, and volatilization, have very small or no isotopic fractionation effects. Thus, CSIA can be used to assess whether an in situ remediation program is successfully destroying contaminants. Evidence of degradation can be seen through spatial trends in isotope ratios. If multiple wells are sampled which are located consecutively downgradient of each other, and degradation of the contaminant of concern is occurring, the isotope ratio is expected to increase along the gradient. Evidence of degradation can also be seen through temporal trends in individual wells, again with an increase in the isotopic fractionation ratio over time. CSIA can also be applied to chlorine and hydrogen. CSIA is discussed in detail in (Allaire 2008).

Dissolved Hydrocarbon Gases (methane, ethane, ethene, acetylene, propane, propene)–Dissolved hydrocarbon gases are typical degradation products of reductive dechlorination of chlorinated ethenes (e.g., PCE), methanes (e.g., carbon tetrachloride), and propanes (e.g., 1,2-dichloropropane). Acetylene is thought to be primarily a byproduct of the abiotic reduction of chlorinated ethenes by reaction with ZVI or ferrous sulfide. The presence of these dissolved gases generally indicates that some complete reductive dechlorination is occurring. Methane can be produced from the contaminant(s), electron donor, other organics, or carbon dioxide. Methane is also the product of methanogenesis–that is, the reduction of carbon dioxide, and in that case is indicative of a significantly reducing environment. Natural gas contains many of these dissolved gases.

Carbon Dioxide (CO_2)–Carbon dioxide is the product of many degradation processes, as well as an electron acceptor in most reducing groundwater environments (methanogenesis). Because it can be simultaneously generated and consumed, it may not provide as good an indication of aquifer conditions as its product, methane.

Magnetic Susceptibility–The presence of magnetite in an aquifer matrix can be an indication of the potential for abiotic degradation, particularly of chlorinated ethenes, to occur via iron minerals. Magnetic susceptibility, given in volume per mass of soil (typically cubic meters per kg), can be measured with a laboratory instrument, or in-well, and the value correlated to a contaminant half-life (Wiedemeier 2017). Magnetic susceptibility can potentially guide a practitioner toward an abiotic remediation approach capitalizing on the naturally occurring iron to facilitate contaminant degradation. It can also be obtained remotely in some cases using geophysical techniques such as induced electromagnetics. Millivolt readings are usually higher in areas where abiotic degradation has occurred, demonstrating a shrinking plume, and may be the “shadow” left behind by a plume’s historic maximum extent.

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Appendix D. Injection Fact Sheets

Table of Contents

D1 Direct Push Delivery Methods

Direct push injection (DPI) methods provide a flexible and cost-effective platform for the injection of remediation amendments into unconsolidated soils. DPI methods use specialized drill rigs to advance hollow steel rods to a targeted injection depth and inject amendments through specialized tooling or open hollow rods. Similar injection methods can be applied using other drilling technologies (for example, cone penetrometer and rotary sonic) that use hollow tooling flush with the side of the borehole.

DPI methods can be used to inject both low and high viscosity amendments. The minimum treatment depth for DPI methods is typically dictated by the depth at which daylighting of amendment to the ground surface cannot be controlled during injection. The maximum treatment depth is typically dictated by the refusal depth during tooling advancement, and this maximum depth is a function of geology in the TTZ, DPI rig size/rated down pressure, tooling diameter, and tooling strength.

D1.1 Types of Equipment

The typical DPI method involves equipping the lead rod with an injection tool (as described below) and advancing the injection tool to the targeted treatment depth. DPI can be performed using either a top-down or bottom-up injection sequence. DPI rigs have a hydraulic power plant that produces a downward force coupled with percussive hammering action to advance rods to depth. Recent advances in DPI equipment (for example, rig and tooling improvements) have allowed DPI methods to achieve successively greater depths.

The direct push drilling provider will typically recommend an appropriately sized DPI rig based on previous site investigations or regional knowledge of the geology. Tracked rigs tend to be more efficient, especially with tight grid spacings and manifolding to multiple locations. The size (height and width) of the rig needs to match the site conditions, and access restrictions should be considered. Depending on the magnitude of the injection program, multiple rigs may be used during implementation to reduce implementation time and limit costs.

Types of injection tooling vary from commercially available products to custom tooling manufactured by DPI drilling providers. Variations in DPI injection tooling can include the diameter of the tooling, the size of holes or slots, and the density of holes or slots in the tooling.

The mechanism of action of DPI tooling can vary. Several typical examples are described below:

- Low pressure ported (slotted) injection tools with inner stainless steel screens can be provided with or without retractable sleeves that protect the screen as the injection tool advances in the subsurface.
- High-pressure ported injection tools are typically more robust in tight formations. The tooling is manufactured with different injection port orientations; for example, some are oriented at 90 degrees, with a port every 6 inches. These tools can also be custom manufactured depending on distribution objectives.
- Pressure-activated injection tools are ported injection tools with a spring-loaded pressure-activated opening device that moves a metal slider to expose the injection ports. They are advantageous in flowing sand conditions and in tight formations.
- Open rods equipped with a tip holder and expendable tip provide a low-cost method of injecting amendments. Upon reaching the targeted treatment depth the expendable tip is dropped or knocked out of the tip holder, and amendment is injected through the open rods as the rod string is raised. This method can be used only for bottom-up injections.

A water-tight seal must be maintained between threaded rod sections, because amendment injections using DPI methods are typically performed under pressure. Most DPI equipment manufacturers recommend use of rubber O-rings between rod sections to form a seal.

Aboveground injection components may include storage tanks, mixing tanks or inline mixers, pumps, injection piping, and injection manifolds equipped with pressure gauges, flow meters, and flow control valves. For simultaneous injections at multiple locations, injection manifolds are typically used to route the flow from the injection pump to several injection rods. Separate flow meters, pressure gauges, and flow control valves on each individual injection line can be beneficial to document injection performance at each location. The specific aboveground injection equipment used at a given site depends upon the site hydrogeologic conditions, the amendment being injected, and the overall targeted treatment footprint.

D1.2 Types of Delivery

DPI methods can be used to deliver both high and low viscosity amendments. Examples of high viscosity amendments include solids, such as ZVI, powdered or activated carbon, calcium peroxide, potassium persulfate, potassium permanganate, gypsum, and lime. The solids can be mixed with other in situ remediation products (for example, ZVI and emulsified oils, and powdered carbon and gypsum) to facilitate packaged remedies. ZVI (micro-scale and larger) must be suspended in a guar gum solution or added by continuous mechanical mixing with water.

High viscosity amendments are typically installed at discrete intervals due to the high pressures needed to force the solids out into the TTZ. If sufficient flow and pressure are not achieved, distribution will be limited and solids can filter out in the formation near the injection tooling.

Low viscosity amendments can also be applied using DPI methods. Typically, these amendments are formulated by diluting a concentrated liquid or solid with water followed by mechanical mixing.

A pump is typically used to deliver amendments to the injection tooling, unless gravity feed injection is feasible. When selecting a pump for DPI, the following criteria should be considered: viscosity/abrasiveness of the amendment, chemical compatibility of the pump internals (that is, wetted components) with the amendment, and estimated injection pressures and flow rates. Pumps typically used for DPI include the following:

- Centrifugal pumps transport low viscosity amendments by the conversion of rotational energy to fluid flow. Centrifugal pumps provide a constant flow rate and work well for high flow rates and low pressures. They are ideal for low viscosity fluids.
- Positive displacement pumps move low and high viscosity amendments by trapping a fixed amount of fluid and forcing that trapped volume into the discharge pipe. Positive displacement pumps are necessary for high viscosity amendments, such as grouts and slurries, but can also be used for injection of liquids. Two common types of positive displacement pumps used for amendment injections are piston pumps and diaphragm pumps. Piston pumps are well-suited for injecting abrasive amendments, and diaphragm pumps can be selected with chemical-resistant wetted components capable of handling highly corrosive amendments.
- Progressive cavity pumps are a special category of positive displacement pump that transfer fluids through a series of small, fixed cavities with the use of a rotor or screw. These pumps can be used to inject both low and high viscosity fluids and are well-suited for injecting abrasive amendments and viscous amendments that are sensitive to shear.

D1.3 Advantages

- Injection points are temporary and the spacing can be adjusted in the field if necessary. Injection point locations, targeted injection depths, and injection rates and volumes can be modified over time to optimize delivery as the TTZ changes size and shape.
- Upon reapplication of bioremediation amendments, there is no concern for biofouling as with repeated injections into permanent injection wells.
- Temporary DPI locations do not require injection well permits for installation or expensive abandonment procedures following injection.
- Injection rates and volumes can be designed to maximize distribution and speed.
- Use of manifolds allows multiple application points to be injected simultaneously, thus improving injection performance and lowering costs, especially where flow rates and/or injection pressures must be limited.
- Low viscosity amendments require less energy to apply and can be more readily distributed in the subsurface.
- High viscosity amendments can be successful on sites with both fine-grained and coarse-grained lithologies.

D1.4 Limitations

- Reapplication requires a DPI operator and injection equipment to mobilize for each event.
- Flow rates into DPI points may be less than those into an injection well.
- Depth and lithology can be limiting for DPI.
- Injections in low permeability zones generally require a higher pressure pump than injections targeting highly permeable zones.
- High viscosity amendments are injected using high flow and high pressure, which can result in daylighting to the ground surface, especially when injections are performed at shallow depths. In some cases, daylighting can be limited by using a smaller lateral spacing (that is, injection grid) between injection points and smaller injection volumes or lower injection pressures.
- High viscosity amendments are not compatible with screened injection tools because of the velocity and pressure needed to force the solids through the screen.
- Injection of high viscosity amendments requires more expertise than low viscosity delivery and verification of amendment distribution can be difficult.

D2 Injection Through Wells & Boreholes

This injection method uses screened wells or open boreholes to distribute liquids within a TTZ or a given water-bearing stratum. This method can either rely on groundwater head difference between an aboveground injection system and the targeted injection interval (that is, gravity injection) or can be performed under pressure using a pump.

Permanent wells for injection applications are constructed with materials appropriate for the geological formation, groundwater chemistry, contaminants present, and selected amendment/amendments. Injection wells are installed and screened within a horizon to directly access the intended interval for injection. When hydraulic conductivities vary by multiple orders of magnitude, shorter screened intervals may improve amendment distribution and contaminant contact. Ultimately the most permeable intervals in contact with a well screen will receive a majority of the injected amendment, so matching the well screen intervals to the targeted injection depths is a critical design parameter.

Although they require a significant up-front investment, permanent injection wells can be more economical for injection-based remedies that span multiple years and multiple injection events, if the treatment zone remains the same and the well spacing does not require adjustments. Although the short-term costs of well drilling and construction are higher than temporary delivery methods (for example, DPI), the reuse of wells during later injection events offsets these costs and the payback period is typically realized after the second or third injection event. Injection wells provide routine access to the TTZ and allow for modification of amendment, dose, and volume to optimize injection programs based on observed performance.

D2.1 Types of Equipment

Injection wells in unconsolidated media are commonly constructed with slotted polyvinyl chloride (PVC) casing and screen, because this material is less costly and more readily available than other materials such as stainless steel. Stainless steel wire-wrapped or vee-wire screens provide greater open area than slotted PVC screens and are designed to minimize biofouling and scaling of the screen, thus requiring less maintenance. Some amendments may react with well materials or may generate elevated temperatures within the well, and these factors should be considered when selecting well construction materials. The presence of a NAPL phase (which may soften PVC) and other contaminant considerations may affect construction material selection. Options for bedrock injection wells include open boreholes providing access to one or more fracture(s) or fracture intervals, or screened wells intercepting fractures to be targeted for treatment. For open borehole designs, the competency of the bedrock should also be considered to ensure that blockages or borehole collapse do not isolate portions of the vertical interval or trap downhole equipment. Although vertical injection wells and bedrock boreholes are most common, injection wells can be constructed in unconsolidated media or bedrock using horizontal drilling methods.

Injections through wells and boreholes use permanent vertical wells, horizontal wells, or open boreholes coupled with aboveground injection equipment. Aboveground injection components may include storage tanks, mixing tanks or inline mixers, pumps, injection piping, and injection manifolds equipped with pressure gauges, flow meters, and flow control valves. Injection piping should be connected to wellhead fittings designed to withstand expected injection pressures. The specific aboveground injection equipment used at a given site depends upon the site hydrogeologic conditions, the amendment being injected, and the overall target treatment footprint.

D2.2 Types of Delivery

This delivery method is often used when multiple injections are anticipated over time, or when targeted treatment depths exceed the capability of direct push drill rigs. When targeting multiple water-bearing zones or thick targeted treatment depth intervals, multiple wells with shorter well screens or nested wells may be required. Injection wells are almost exclusively used when continuous recirculation of amendments is planned.

Amendment injections into wells and boreholes under gravity can be successful in TTZs with moderate to high hydraulic conductivity; however, injection flow rates can be increased by applying direct pressure to the wellhead. Most injection well annular seals are constructed using hydrated bentonite or neat cement, which are essential to sealing off the well screen and filter pack and preventing daylighting around the well annulus to ground surface. If excess wellhead pressure is applied, well seals can become compromised, resulting in permanent damage to the well.

Inflatable packers can also be used to isolate a target injection zone. This method is commonly used in open bedrock boreholes to target injections into specific fracture intervals. Packer use in screened wells should be implemented with caution due to the potential to damage the well. Following treatment, properly installed injection wells may be used for monitoring for parameters other than contaminants. However, in some cases regulatory agencies allow injection wells to be used as long-term monitoring wells if the groundwater geochemical parameters have returned to baseline conditions (that is, preinjection) and the injected amendments have been fully used.

D2.3 Advantages

- A system of wells can be used for pilot testing, single full-scale injections, and multiyear injection programs without the need for additional infrastructure costs, with the exception of any additional wells or boreholes needed for future amendment distribution.
- Injection wells and boreholes can help maintain control of the treatment area using either a recirculation scheme or a push-pull scheme, which can enhance amendment distribution, increasing the ROI, and also limit displacement of contaminants beyond the treatment area during injection.
- Multiple injections events can be performed without the need for additional drilling unless remaining contamination can’t be contacted by existing well locations.
- Wells and boreholes can be used to provide real-time feedback during injections, including amendment distribution (ROI), dose within the treatment area, and water level response, all of which allow effective field adjustment of mix ratio, injection pressure, etc. Amendment concentrations can also be monitored over time to assess amendment longevity in the subsurface.

D2.4 Limitations

- Injection through wells and boreholes creates a larger and semipermanent treatment footprint compared to more agile and mobile DPI. The decision to add injection points requires the time, permitting, and funding associated with well installation.
- The effectiveness of treatment with this delivery method may be limited in lower permeability formations (for example, silts and clays) due to challenges with distribution.
- Although depth is not limited, well installation cost can be prohibitive and the need for eventual well or borehole abandonment should be considered.
- In the case of wells, the types of amendments are limited to those that are soluble or contain relatively small solids that are smaller than the well screen slot size and formation pore throat size.
- Fouling of the well screen may occur during or after injection, reducing the flow rates and increasing pressures (in the case of pressurized injection) during future injection activities. One method to minimize fouling is to include chase or flush water following amendment injection to push the injected amendment beyond the sand pack and into the formation.
- Injection pressures are limited to those that can be safely withstood by the well seal. Excessive injection pressure can damage the well seal and lead to daylighting of amendment. Injection pressure limitations due to well seal concerns may result in reduced injection flow rates and/or poor amendment distribution.
- Targeting vertically thick or heterogeneous TTZs with nested injection wells may result in high costs.
- Once a well is used for injection, it is generally not acceptable for use as a monitoring well for compliance purposes, but may be used for other purposes such as measuring reagent persistence.

D3 Electrokinetics Delivery Methods

Electrokinetics uses electric currents to facilitate transport of remediation amendments and/or contaminants within the saturated zone. Electromigration is the movement of charged (ionic) molecules through the aquifer formation between electrodes. It is induced by an electrical current applied to the electrodes. Positively charged ions (for example, many metals and certain organic compounds) migrate toward the cathode, while negatively charged ions (for example, anions such as nitrate, permanganate, and certain metal complexes and organic compounds) migrate toward the anode. Transport of nonionic species (such as many chlorinated solvents) is enhanced by electroosmotic processes, which induce pore fluid migration between electrodes. The combination of electromigration and electroosmotic processes makes electrokinetics a potentially effective method for both amendment and contaminant transport in some low-permeability formations.

D3.1 Types of Equipment

The fundamental types of equipment required for all applications are electrodes (anodes and cathodes) and a low voltage, direct current power supply. Additional equipment required depends upon the specific design of the remedy. For example, an extraction system may be required to extract groundwater containing mobilized contaminants, whereas a liquid injection system may be required to prepare and supply an amendment such as a bioremediation nutrient, chemical oxidant, or surfactant.

D3.2 Types of Delivery/Electrodes

Electrokinetic methods require placing positively charged (anode) and negatively charged (cathode) electrodes in the subsurface. There are many ways to deploy electrodes, and the construction method and soil type impact the orientation of the electrodes. Methods for electrode installation include wells, vertical trenches, sheet piling, injected solids, and directly installed probes, as described below:

- Well installations: Electrodes are placed directly in wells. In addition to housing electrodes, the same wells can be used for injection of electrolytic solutions and other amendments and/or extraction of contaminated fluids.
- Vertical trenches and sheet piling: Steel sheet piling directly driven into the ground can serve as electrodes. Electrodes can also be placed into permeable barrier zones that intersect the water table and are filled with sand or other reactive or nonreactive solids. Fluids can also be injected and/or extracted from the trenches.
- Injected solids: Hydraulic slurry injection can be used to create horizontal or vertical lenses of conductive material at depths greater than those that can be trenched; the lenses are then converted to electrodes by drilling wells to intercept the lenses and installing electrodes in contact with the conductive material.
- Directly installed probes: Rods can be pushed directly into the ground to serve as electrodes.

D3.3 Advantages

- Electrokinetic methods can be particularly effective for enhancing amendment and/or contaminant migration through low-permeability soils.
- A wide range of possible construction orientations exists.
- The electrode can be switched from anode to cathode.
- A wide range of amendments and contaminants can be targeted—for instance, organics (dissolved and/or NAPL), metals (for example, uranium, chromium, etc.), anions (for example, ammonia, sulfate, etc.), and oxidants (permanganate, persulfate, etc.).

D3.4 Limitations

- Amendments and/or contaminants migrate in the dissolved state; sorbed-phase contamination can be addressed only by desorption or by direct reaction with injected amendments.
- Migration rates of amendments and/or contaminants are slow as a function of the tight formation and low hydraulic conductivity, which is mitigated by designing the installation with close spacing.
- Electrolysis reactions on the electrodes create acidic conditions at the electrode site (anodes), which may migrate with groundwater and may also degrade the electrodes (this could also be an advantage in some circumstances, for example, to induce mobilization of certain metals).
- Some metals may precipitate due to pH shifts or oxidation reactions at the electrodes.
- Electrokinetics may affect other soil or aquifer properties in addition to pH, including soil moisture and microbial biomass.
- Buried metallic structures or other conductive materials may affect voltage gradients and corresponding amendment and/or contaminant migration rates or pathways. In addition, any affected soil or aquifer property (for example, pH) could potentially cause damage to subsurface structures.
- Although electrokinetic processes can be used in higher permeability soils, these processes are likely less efficient and more costly than traditional amendment injection and/or recirculation methods.
- Fluid injection and recovery may be required even if remediation processes occur strictly in situ.

D4 Solid Injection Principles

D4.1 Fracture-Based Delivery

Soil and bedrock fracturing offers the ability to create new permeability structures within a targeted formation to enhance contaminant removal or their in situ destruction. Among the fracture design specifications that can be manipulated (and thus optimized) are fracture content (amendment for in situ reactions or material to enhance permeability), location, depth, extent, aperture, and orientation. Some fracture design elements can be controlled (for example, fracture content, injection location, initial depth), but the extent of fracture propagation and its aperture or orientation from the injection point is less certain and can vary based on delivery techniques. The primary methods for creating fractures are hydraulic and pneumatic. For hydraulic fracturing the carrier media (used to produce the fractures) is a liquid, while for pneumatic fracturing the carrier is nitrogen gas. Although the carrier media is the primary difference between these two methods, the injection tooling for each fracturing method is also typically different. Furthermore, a wide range of hydraulic fracturing tooling is used. The different tooling provides varying degrees of fracture control and orientation, resulting in more or less control of the delivered materials.

D4.2 Governing Principles

Both hydraulic and pneumatic fracturing techniques apply pressure sufficient to overcome the natural matrix cohesion (including overburden pressure) and cause the matrix to fail and fracture. Fractures can be propagated using multiple techniques, including through temporary injection borings or DPI rods. When temporary borings are used, the fracture tooling is advanced downward through the boring to the desired depth. A high pressure is applied to notch the casing and subsequently advance the injection media into the surrounding formation. When direct push rods are used with injection tooling advanced at the end, once the tooling is at the desired injection depth, the pressure is increased to a magnitude sufficient to overcome the stress and elasticity of the surrounding formation with either water or liquid amendments. The net injection pressure is modulated at the surface via injection pump controls.

The ability to develop sufficent pressure to initiate and propagate a fracture implies that the fluid is delivered to the formation at a rate greater than the accompanying Darcy flow into the formation. The advancing fracture results in dilation with an overall size that depends on the elastic modulus of the deformed formation. The deformation surrounds the fracture in three dimensions and the extent of deformation is affected by injection depth, injection volume, and geology, and may range from no measurable deflection to several millimeters.

Once the fracture is established, amendments or a propagation material migrate through the newly created void space outward into the formation. Fracture extension away from the injection point is controlled by the energy losses along its length. The stress intensity at the leading edge of the fracture is responsible for overcoming the native matrix strength, which consumes energy. Even in nonconsolidated strata where the cohesion is negligible (for example, sand and gravel), the extention of the fracture tip does require rearrangement of the grains, which also consumes energy.

As it advances, the fracture may intersect natural flow paths that deflect the fracture direction and can result in leak off from the original intended fracture interval. This mechanism can have unintended consequences, such as the transport of injected materials to land surface (daylighting) or to unintended vertical intervals. The degree of leakage is controlled by relative permeability effects distributed along and near the fracture faces.

Fracture orientation will follow the path of least resistance, which could be through more permeable soil materials than the intended fracture depth, or to shallower intervals (or even land surface) with low overburden pressure. The fracture emplacement processes described above can influence fracture propagation independent of the subsurface matrix structure or geology. As an example, postfracture excavations have shown induced fractures to cut across multiple geological units while maintaining a mildly dipping trajectory. In other cases, induced fractures will follow a unit boundary that they encounter.

Fracturing does not change the pore structure of the surrounding matrix; permeability of the existing formation does not change. Conversely, establishing new flow paths is what allows for overall transmission of fluid and is ultimately what supports contaminant remediation. These flow paths will convey contaminants and water at different rates than the native surrounding material, thus serving to focus flow through intervals in which amendments have been emplaced. Diffusion and dispersion enhance amendment distribution or geochemical changes from the fractures into more of the contaminated subsurface.

D4.3 Differences Between Hydraulic and Pneumatic Fracturing

Pneumatic fracturing and hydraulic fracturing differ principally in the viscosity, compressibility, and density of the fluid used to apply the pressure. Nitrogen, which is used for most pneumatic fracturing, has viscosity of 0.018 cp while the high viscosity non-Newtonian amendments used to create many hydraulic fractures can have effective viscosity on the order of 200 cp. Gases are compressible, and water/aqueous slurry is incompressible. Over the range of typical fracturing pressures encountered in environmental work, the compressibility of gases varies from approximately 5×10^{-7} Pa^{-1} to 2×10^{-8} Pa^{-1} while compressability of typical solutions injected is roughly the same (5×10^{-10} Pa^{-1}) as that of water. Although the density of nitrogen used to create fractures is on the order of 1 kg/m^3, the density of water is a thousand times greater. The multiple order of magnitude contrast between the properties of nitrogen and water explains differences in the functions and capabilites of the two methods.

The most significant consequence of the viscosity difference is that leak off is much greater with pneumatic fracturing. It can be sufficiently great to arrest propagation of the parent fracture, leading to non-uniform or partial fracturing around the well and limited overall fracture extension. Since leak off is greater during pneumatic fracturing than during hydraulic fracturing, fluid needs to be delivered to the formation at a greater rate to maintain the pressure necessary to dilate and extend the fracture. In most cases, the fracture is then filled with the selected amendment, which is often a liquid or solid slurry, and often a proppant such as sand. The advantage of this phenomenon is delivering treatment material throughout the targeted formation and potentially reducing the transport between the fracture and the groundwater, as well as affected soils that could otherwise contribute to back-diffusion.

The greater viscosity of hydraulic fracturing fluids not only suppresses leak off but also, in conjunction with its greater density that counters bouyancy effects, enables the transport of large amounts of solid amendments such as ZVI in a hydrated guar gum solution. Active amendment from these materials then migrates with the surrounding groundwater and can intersect contaminants. If the solid is slightly soluble in groundwater, the fracture can act as a long-term in situ passive source of amendment. Distribution mechanisms of amendment away from the fracture can involve advection as well as diffusion and dispersion transport processes. Even if the solid has limited solubility, it may serve well in low-permeability media. If the permeability contrast between the injected treatment material creating the fractures and the surrounding formation exceeds two orders of magnitude, the fracture will act as a preferential flow path and groundwater flowing through it can be remediated much as in the case of a permeable reactive barrier (PRB).

Descriptions of the tooling and methods used for hydraulic and pneumatic fracture are included in Sections D5 and D6. The applicability of these methods to specific site conditions is discussed in the following section.

D5 Hydraulic Fracturing-Based Delivery Methods

Fracturing occurs when a fluid is injected into a soil or rock formation at a rate faster than can be accepted by the formation via Darcy flow. If a principally liquid fracturing fluid is injected at such a rate, hydraulic fracturing occurs. The mechanisms of hydraulic fracture formation, which follow from fundamental characteristics and properties of solid materials, dictate that fracturing creates planar features that extend away from the point of injection. When granular solids such as sand or iron grains are included in the fracturing fluid, the fracture can persist as a new structure of desired size and location in the subsurface. Further, the predictability of fracture forms can be improved by creating a void (commonly called a notch or kerf) at the point of injection, prior to injecting the fracturing fluid, with a geometry intended to direct the initial fracture formation (that is, nucleation). Common terms applied to these methods in the environmental remediation industry include hydraulic fracturing, emplacement, controlled fracturing, jet injection, jet-assisted fracturing, jet fracturing, and slurry emplacement.

Hydrology governs the interaction of contaminants with the injected material, and optimal remediation is accomplished by balancing the treatment characteristics of injected amendments with the design of a hydraulic fracturing program. Considerations for the design of a hydraulic fracturing program may include manipulating the fracture form (that is, lateral extent, thickness, orientation, amendment loading) and varying the fracture layout (that is, X-Y location, overlap between adjacent fractures, fracture spacing with depth). For horizontal fractures consider a design with lateral fracture extents of 5–30 m. The smaller the lateral extent, the more controlled the fracture dimensions, and the larger the extent, the higher the uncertainty of the fracture location. In addition to the horizontal fracture extent, the horizontal fracture design should consider the fracture thicknesses. Thin fractures (for example, from 1 to 10 mm thick) can penetrate low-permeability layers better, but may limit the volume of amendment that can be delivered to the subsurface. Thicker fractures (for example, 10–30 mm thick) enable a higher volume of amendment to be delivered to the subsurface; however, ground surface uplift should be considered. Both horizontal and vertical fractures can be created using different fracturing methods, while working within the confines of the formation characteristics.

D5.1 Types of Equipment

Fracturing methods can be applied directly to a shallow formation with standard direct push equipment. Creating deeper hydraulic fractures requires more robust direct push equipment or sonic tooling. Alternatively, dedicated wells of solid PVC (or steel) casing can first be installed using sonic, auger, mud rotary, or air rotary drilling methods. The solid casing is then cut at selected elevations to allow one or more fractures to be created. In very competent formations, such as crystalline bedrock, fractures can be created in open boreholes. A key feature of robust fracturing methods is the ability to focus fluid pressure on a small portion of the target formation. Thus, best practices for direct push use a short section of borehole, whereas straddle packers are used in wells and open-hole settings.

Hydraulic fracturing requires a pump that can develop both a sufficient pressure to overcome the strength of the target formation and an adequate injection rate. Typically, positive displacement pumps are used, and when granular solids are included, the pump must be mechanically compatible. Preparing and handling fracturing fluid may require specialized mixing equipment as well as bulk solids handling equipment. Mixing equipment and pumps are typically provided by a dedicated service contractor. Creating a notch prior to injecting the fracturing fluid can be completed using physical methods (that is, cutting) or high-pressure water jetting.

D5.2 Types of Delivery

As described above, a variety of drilling methods can be used to apply hydraulic fracturing. These methods include direct push, sonic, auger, mud rotary, or air rotary. Injection manifolds can be useful for large numbers of injection points already fractured, wells completed, and high volumes of liquid amendments. The manifold routes the flow from the injection pump to several injection rods simultaneously. A separate flow meter and pressure gage on the main line and each injection line can be beneficial to document injection performance at each location.

D5.3 Advantages

- Hydraulic fracturing provides the opportunity to deliver very large amounts of solid material into the target formation in a relatively short amount of time. Such a large dose may be designed to address significant contaminant mass, passively extend the duration of remediation (after emplacing large amounts of amendment in fractures), or both.
- Hydraulic fracturing techniques can be applied in almost any geologic formation, including bedrock.
- Hydraulic fracturing can be used to deliver remediation amendments, to enhance permeability by injecting sand or other granular materials, or to achieve both.
- Although noncohesive materials (for example, coarse sands and gravels) do not strictly fracture, the application of fracturing methods often results in similar distributions of injected material, thus supporting in situ remediation processes.
- The planned or deliberate application of hydraulic fracturing methods ensures that material (amendments or proppants) will be delivered in a controlled manner to the target zones. Unplanned or inadvertent fracturing, often occurring during DPI of liquids, can result in poor distribution of remediation amendments and amendment surfacing.
- The direction and magnitude of micro ground surface deformations or “tilt” can be qualitatively measured by tiltmeters, elevation surveying on the ground surface, and downhole pressure readings at monitoring well locations. A network of tiltmeters determines the dip angle, orientation, and extent of fractures in the subsurface. This information can be input into an interactive 3-D model to visualize the fracture network in the treatment zone.

D5.4 Limitations

- Optimal practice of hydraulic fracturing requires specialized mixing equipment, pumps, and injection tooling in combination with the experience of a dedicated service contractor.
- Hydraulic fracturing generally cannot be deployed in existing wells, although open boreholes in competent bedrock can be used.
- Hydraulic fracturing may not be viable in very shallow settings, especially if the overburden is loose or otherwise cannot contain the fracture in the subsurface.
- Surface deformation can occur during hydraulic fracturing, so the injection program must consider the potential for impacts to shallow and aboveground infrastructure (for example, buried utilities, buildings, railroad tracks, etc.).

D6 Pneumatic Fracturing-Based Delivery Methods

Fracturing opens new space within geologic formations that can be exploited to enable or enhance in situ remediation in two ways. First, permeability can be enhanced to the extent that the new permeable space provides flow pathways and improves well performance (either extraction or delivery). Second, filling the newly created space with reactive material can establish in situ remediation that proceeds passively without further operations at the surface. This second feature also allows use of reactive granular solids that can not penetrate the pore space of the formation or otherwise contact the contaminants.

Pneumatic fracturing uses nitrogen gas as the fracturing medium. In contrast, hydraulic fracturing relies on aqueous-based fluids, which have viscosity, density, and compressibility orders of magnitude different from gases. Pneumatic fractures can be used to enhance well performance, although solid particles, such as ZVI sand, are commonly entrained in the flow to create in situ reactive treatment zones.

D6.1 Types of Equipment

Surface equipment for pneumatic fracturing can include reservoirs for compressed gas (typically tube trailers or similar compressed gas transport vehicles), manifolds to manage the gas supply and incorporate any admixing material whether liquid or granular solid, bulk storage vessels (tanks, bins, or hoppers) and handling equipment, pumps and hoses, and instrumentation. Surface equipment usually can be provided as a package by the injection contractor.

Drilling equipment is needed to advance the tooling downhole. Downhole tooling is developed around an injection nozzle assembly positioned between straddle packers. The packers are used to isolate target intervals, and an initiation notch is cut with high gas flow and/or pressure to facilitate fracture nucleation. Vertical separation between target intervals depends on the remediation amendment used, the volume and dose of amendment to be delivered to the subsurface, and the lithology. New techniques for combining sonic drilling with delivery can enhance application efficiency by potentially reducing the time at sites where well casings were required to keep the borehole open.

D6.2 Types of Delivery

Pneumatic fractures usually are created from open or cased boreholes. Consider using pneumatic fracturing in boreholes with a minimim of 4-inch diameter to house the straddle packers. Usually, a bottom-up approach is followed. Stiffer formations that offer stable open borehores can be addressed with conventional fracturing practices. Formations that slough or exhibit charactersitics of flowing sands require more complicated integration of the drilling technique with the fracturing process. There also have been applications where pneumatic fractures are created through DPI tooling.

D6.3 Advantages

- The volume and flow rates used in pneumatic fracturing can create a haze of newly opened fractures that contribute to fluid flow. This enhanced fracture density can reduce the time frame for diffusive transport between fractures and thus the time frame for remediation.
- The open apertures created by pneumatic fracturing offer unimpeded flow paths that can persist after the fracturing process because irregularities along the fracture surface and shifting of the geologic medium prevent closure.
- Pneumatic fracturing does not introduce additional water into the formation, which may prove critical where water might block pores or otherwise interfere with flow of free product or air in the contaminated porous media.
- The direction and magnitude of micro ground surface deformations or “tilt” can be qualitatively measured by tiltmeters, elevation surveying on the ground surface, and downhole pressure readings at monitoring well locations. A network of tiltmeters determines the dip angle, orientation, and extent of fractures in the subsurface. This information can be input into an interactive 3-D model to visualize the fracture network in the treatment zone.

D6.4 Limitations

- Although pneumatic fracturing can be performed in almost any geologic matrix, its application in bedrock is limited by pressure and compressibility to only the most weathered portions, where the primary function of the fracturing events is to dilate and clear loose debris from existing natural fractures.
- Fracture growth may be arrested before the desired extent is achieved in the process known as leak off,

accomplishing only partial fracturing.

- Borehole collapse onto the fracturing setup and sealing issues can be problematic. Soil collapse would require retrieval of the packer assembly and reaming out after collapse or overdrilling if the annular seal is lost.
- High pressures present health and safety challenges. The requisite volume and pressure of gas (nitrogen) usually results in deployment of one or more compressed gas tube trailers. Packers and hoses need to be sufficiently robust to contain injection pressure.
- Pneumatic delivery, due to a unique injection nozzle, typically is not applied through direct push tooling and primarily is used in open bore holes.

D7 Permeable Reactive Barrier Construction

PRBs are a type of subsurface reactive treatment zone created by placing permeable reactive material in the subsurface to passively intercept and treat affected groundwater (ITRC 2011). As contaminated groundwater flows through the PRB under native or induced hydraulic gradients, the contaminants are sequestered or transformed to meet remedial action objectives. PRBs are constructed across the plume perpendicular to the groundwater flow direction. They can be placed near source areas for isolation, as well as downgradient to control plume expansion. To be effective, the barrier must be designed and placed to prevent short-circuiting and groundwater mounding or diversion, and to account for hydrogeologic and geochemical conditions. The latter barrier is used so that the appropriate type and amount of amendment, generally measured by barrier thickness and residence time, is emplaced. A thorough understanding of site hydraulics is critical to successful PRB application.

While PRBs can be constructed using multiple, closely spaced amendment injections, this section focuses primarily on methods other than vertical injection points for emplacing the PRB.

D7.1 Types of Equipment

PRBs that are not injected/fractured generally require large machinery and extensive site access to install. The type of equipment depends upon the depth required, geologic materials encountered, and volume of amendment to be placed. Excavators, pile drivers, trenchless PRB installation technology (for example, continuous pass trenchers), and injection/fracture placement technology have been used to install reactive media and create PRBs.

D7.2 Types of Delivery

The most common noninjected/fractured PRBs are shallow (less than 35 ft below grade) and are installed using an excavator to open a trench and allow placement of granular treatment media. Excavation support (for example, biopolymer slurry or shoring) is generally required to maintain the open trench pending backfill. Excavation becomes more challenging and expensive with depth. If site conditions allow, a trenchless technology combines excavation and backfill into a single step, eliminating the need for supplemental excavation support. Depending on the method used for trenching and the reactive media, horizontal delivery piping can be added to the PRB backfill to rejuvenate it with additional amendments over time. Large-diameter augers have also been used to place amendments in vertical columns in close proximity to create a continuous PRB.

Injection or fracturing techniques are also used to construct subsurface PRBs. Although these placement techniques allow for greater depth and less short-term site disruption, they require a smaller size amendment (micro, nano, or liquid), typically resulting in more frequent replacement, unless long-lasting amendments are injected (for example, ZVI, emulsified vegetable oils). Permanent or temporary injection points are used to place reactive materials into the subsurface under pressure. The injection points are spaced to provide overlapping radii of influence between them, forming a treatment zone. Injection wells can be placed either vertically or horizontally, with the latter providing options for delivery beneath buildings.

Groundwater flow through PRBs can be induced by constructing them to have a higher hydraulic conductivity (K) than the surrounding aquifer material. Groundwater flow through PRBs can be accomplished using impermeable wings (slurry walls or sheet piles) on either side of the PRB to direct groundwater to flow through the reactive materials. These configurations are referred to as funnel and gate. The sequence in which the reactive and impermeable media are placed should be considered within the larger PRB design. Site hydraulics and anticipated treatment media replacement should be considered when evaluating continuous treatment zones versus funnel and gate configurations.

D7.3 Advantages

- Well designed and properly constructed PRBs are effective at cutting off plumes and protecting receptors.
- They require little to no long-term operation and maintenance requirements, except where biofouling occurs.
- Even when the source cannot be effectively addressed, a PRB can provide long-term risk mitigation and receptor protection.
- A PRB can be a critical component of a monitored natural attenuation strategy for groundwater by cutting off the source, leading to shrinking of the plume.
- A PRB can be designed to passively treat many different contaminants.
- Often PRBs are constructed with low-cost materials such as mulch.
- Many PRB designs incorporate a screen or slotted pipe that can be used to replenish a substrate.
- Decommissioning a PRB is typically low cost unless the reactive or impermeable media need to be removed.

D7.4 Limitations

- PRBs do not treat the source of contamination and therefore need to be maintained until the source is depleted or concentrations in the contaminant plume fall below cleanup criteria.
- Although PRBs may require minimal long-term operation and maintenance, the capital cost may be higher than other remedial technologies. Amendment longevity and replacement techniques are critical to understanding life cycle costs.
- Short-circuiting (flow around) the PRB is a common challenge. Detailed understanding of geology and hydrogeology is required. Keying the PRB into a confining layer can prevent underflow.
- Robust construction quality assurance is required to achieve the proper installation. Because site heterogeneity is often encountered during installation, an adaptive management plan (design modifications based on observed field conditions) is recommended.
- To engineer around uncertainty, PRBs may be designed conservatively, generally in terms of thickness. Thickness, depth, and longevity are key cost components for a PRB.
- Changes in groundwater characteristics and impacts to secondary water quality immediately downgradient of PRBs may limit use. Also, PRBs may clog over time, exacerbating short-circuiting and limiting treatment capacity.

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Appendix E. Case Studies

E-1. In Situ Biological and Chemical Reduction of Hexavalent Chromium and Perchlorate

Location
Black Mountain Industrial Complex, Henderson, Nevada

Reference Material
Groundwater Bioremediation Treatability Study Results Report

Contaminants
Hexavalent chromium and perchlorate

Regulatory Phase
Remediation investigation and feasibility study (RI/FS); bench and pilot study

Amendment(s)
Emulsified vegetable oil (EVO), industrial sugar wastewater, a mixture of EVO and industrial sugar wastewater, and molasses and calcium polysulfide

Remedial Technology
In situ bioremediation and chemical reduction with source control

Site Description and Approach

Site Description:
Alluvial and lacustrine sediments

Approach:
The main objective of the study was to evaluate the feasibility of remediating perchlorate in groundwater via bioremediation using injection wells. The site has been through pump and treat since 2001. The perchlorate mass removal efficiency in the downgradient plume area is very low because of much less concentration of perchlorate and much higher groundwater production rate compared to the source area. The in situ bioremediation treatability study provided information supporting the final remedy selection. This treatability study is one of several planned treatability studies. The test site was chosen because of its relatively low perchlorate concentration and fast groundwater flow velocity. The study followed detailed site characterization, bench-scale study, and field implementation. All required permits, such as a property access permit and a UIC permit, were obtained for the study. Monthly progress reports and milestone presentations of the results were implemented to monitor project progress and to make necessary modifications.

Optimization/Lessons Learned
A CSM based on detailed or high-resolution site characterization is strongly suggested. The clay has required more attention because of its critical role in hydraulic properties and binding properties with injected substrates. Groundwater flow velocity is one of the most important parameters and must be determined before the injection. Besides targeted contaminants, other chemicals subjected to biodegradation were well defined and their behaviors and equivalent electron donors determined during the bench-scale study. The substrate injection will be done multiple times. Parameters such as dissolved oxygen, ORP, targeted contaminant concentrations, total organic compounds, and porosity are frequently monitored. The effectiveness is quantified against the baseline conditions defined during the site characterization.

Summary of Results
The test site is predominantly gravel and sand, with minor fractions of silt and clay. Groundwater flow velocity averaged 32 feet per day (geometric mean value determined from hydrogeological testing). Bench-scale studies (both batch microcosm

and column tests) were performed and indicated that EVO has the ability to create and sustain reducing conditions in groundwater and that native microorganisms can use the EVO to biodegrade perchlorate quite effectively. Nitrate biodegradation (denitrification) generally preceded perchlorate biodegradation; however, in the presence of the carbon substrate and once microbial acclimation occurred, both of these were simultaneously biodegraded. Column studies, which simulated field groundwater flow conditions, demonstrated that perchlorate biodegradation also occurred effectively at high velocity flow rates. Because of the presence of nitrate in groundwater, nitrogen supplementation as a micronutrient was not deemed necessary. However, the augmentation of phosphorus as a micronutrient was shown to reduce acclimation time for the onset of perchlorate biodegradation.

Three injection wells were installed in a single transect configuration in the field test area. In addition to the injection wells, a network consisting of nine monitoring wells was installed at locations both upgradient and downgradient of the injection well transect to determine the effectiveness of the groundwater bioremediation treatability study. Following completion of well installation, two carbon substrate injection events were performed approximately 3 months apart. Weekly, biweekly, and monthly groundwater monitoring was performed throughout the study following injections. Results from the field treatability study indicated that groundwater is quite amenable to bioremediation of perchlorate and other electron acceptors and co-contaminants such as chlorate and nitrate via the addition of EVO. The injection of EVO created an anaerobic biologically active zone of enhancement within the TTZ that resulted in perchlorate biodegradation.

Also, as observed in the laboratory studies, denitrification occurred very rapidly and was comparable to perchlorate biodegradation. Perchlorate biodegradation followed denitrification and, once initiated, the two reductive processes were observed to occur concurrently at locations that recorded the most significant geochemical response to carbon substrate injections. Several of the monitoring wells attained perchlorate reductions greater than 90% during the study. The zone of influence of perchlorate biodegradation extended up to 250 feet downgradient of the injection transect. First-order perchlorate biodegradation rate constants were estimated to be between -0.25 day^{-1} and -0.51 day^{-1} under optimal conditions. Due to these high biodegradation rates, perchlorate concentrations decreased very rapidly in several wells following microbial acclimation. Mass removal estimates were calculated using the lower, midrange, and higher estimates of hydraulic conductivity, gradient, and total porosity. This resulted in an estimated perchlorate mass removal during the study that likely ranged from 4.1 to 17.4 pounds per day. These rates equate to a total perchlorate mass removal during the 6-month time frame of 689–2,923 pounds.

E-2. Strontium-90 Apatite Permeable Reactive Barrier

Location
Hanford, Richland, WA

Reference Material
Calendar Year 2016 Annual Summary Report for 100-NR-2 Groundwater Remediation

Contaminant
Sr-90

Regulatory Phase
Full-scale, pilot-scale, and monitoring

Amendment(s)
Calcium chloride, trisodium citrate, sodium phosphate, calcium-citrate-phosphate

Remedial Technology
Permeable reactive barrier

Site Description and Approach

Site Description:
Fluvial—lacustrine and glaciofluvial sediments

Approach:
Jet injection of phosphate solution during pilot hole drilling phase in fluvial-lacustrine and glaciofluvial sediments; injection of preformed apatite with the phosphate solution as a carrier fluid; precipitation of additional apatite from the phosphate solution, potentially using the preformed apatite as a seed crystal to initiate precipitation; adsorption of Sr-90 by the apatite

surface (new Sr-90 migrating into the treated zone from upgradient sources resulting from fluctuations in river stage); apatite recrystallization with Sr-90 substitution for calcium (permanent); radioactive decay of sequestered Sr-90 to Y-90 to Zr-90 in apatite.

Optimization/Lessons Learned

Decreasing 100 mM phosphate formula to 40 mM to reduce initial Sr-90 mobilization, increase injection volume proportionally to achieve at least 3.4 mg apatite per gram of sediment; phased deep and shallow zone injections from upriver wells to downriver wells; river stage affects injection emplacement.

Summary of Results

Sr-90 concentrations have been reduced by 71–98%.

E-3. Rapid Site Closure of a Large Gas Plant Using In Situ Bioremediation Technology in Low Permeability Soil and Fractured Rock

Location

Hanford, Richland, Washington

Reference Material

Site Closure of a Large Gas Plant Using In situ Bioremediation Technology in Low Permeability Soil and Fractured Rock

Contaminants

LNAPL and aqueous BTEX

Regulatory Phase

State remedial action plan

Amendment(s)

BOS 200

Remedial Technology

In situ granular activated carbon with cultured microbes, electron acceptors, and nutrients

Site Description and Approach

Site Description:

Subtle facies changes in overlying, low permeability soil and thin-bedded planes with complex fractures in highly weathered bedrock resulted in solute concentration that varies by orders of magnitude in distances of only several millimeters.

Approach:

The site was subdivided into six regions, based on constituent concentrations. Treatment was implemented in three phases over a 15-month period. Approximately 4,800 injections were completed at 1,230 locations throughout the 30-acre plume. The remedy consisted of 185,875 pounds of carbon slurry, 5,650 pounds of supplemental sulfate (gypsum), and 352 gallons of microbes.

Optimization/Lessons Learned

None Available

Summary of Results

The initial remedial action plan prepared by the previous contractor and submitted to the state was to install a soil vapor extraction and groundwater recovery and treatment system. Instead, an in situ carbon-based injection program was set up to expedite remediation for pending property sale. The remedy included granular activated carbon injected with cultured microbes (facultative microorganisms), electron acceptors (nitrate and sulfate), and nutrients (phosphorus and nitrogen) designed to biodegrade BTEX compounds. A high-resolution quantitative data assessment was used to characterize plume strength and geometry. The revised CSM was used to apply continuous soil and groundwater data to develop a discrete remedial design and inject carbon-based slurry into the complex low permeability subsurface in six regions of the 30-acre site based on constituent concentrations. The treatment took place in three phases over 15 months with complete confirmatory and performance borings to observe remedy distribution and evaluate effectiveness of remedy, adjusting subsequent injections while using analysis of groundwater samples and calculating mass reduction. This iterative sequence was completed until the cleanup goals were achieved.

E-4. Performance of Injected Powdered and Liquid Activated Carbon at a Petroleum Hydrocarbon Site

Location
Unknown

Reference Material
Activated Carbon-Based Technology for In Situ Remediation

Contaminants
LNAPL & DNAPL; BTEX

Regulatory Phase
Comparison study

Amendment(s)
Powdered and liquid activated carbon activated with sulfate or other oxygen-releasing compounds

Remedial Technology
Subsurface injection

Site Description and Approach

Silty sand aquifer

Optimization/Lessons Learned
Geochemical and microbial monitoring of the groundwater over 24 months indicated clear difference in behavior of the groundwater chemistry over short and long term.

Summary of Results
None Available

E-5. Lawrence Livermore National Laboratory—Annual Groundwater Report

Location
Multiple

Reference Material
Lawrence Livermore National Laboratory, Groundwater Project 2014 Annual Report

Lawrence Livermore National Laboratory Compliance 2018 Annual Monitoring Report Site 300

Contaminants
Aqueous VOCs

Regulatory Phase
Treatability test

Amendment(s)
Zero-valent iron

Remedial Technology
ISCR with source control

Site Description and Approach

Site Description:
Multiple hydrostratigraphic units were evaluated for each LLNL site. The sites include low permeability silt- and clay-rich

sediments, depending on the site.

Approach:
In 2007, DOE/LLNL developed the Source Area Cleanup Technology Evaluation Team approach to identify targeted remediation strategies for plume sources using technologies via treatability studies based on:

- systematic characterization and cataloging of representative macroscopic features of each source area (for example, dimensions of the source area footprint, representative hydraulic conductivity, mean ambient hydraulic gradient) as permitted by the available data
- development of a compartmental screening model based on those data that capture the salient VOC mass and concentration-controlling parameters characteristic of the source areas
- utilizing the compartmental model to simulate the potential response of source area VOC distribution to various source area remediation approaches that correspond to changes in key model parameters (for example, mechanical fracturing to increase average hydraulic conductivity)

Optimization and Lessons Learned
A point to be learned is that LLNL is using source area cleanup technology evaluation to determine use of ZVI in the hotspot source area but similarly has been using in situ bioremediation at Heliport source area as well as thermal and fracturing methods in efforts to remediate complex subsurface source areas and groundwater zones. LLNL subsurface is composed of many subsurface zones, which LLNL evaluated as hydrostratigraphic units, adding to complexity of subsurface groundwater and contaminant transport. In the case of the ZVI site, use of a solar-powered purging system in multiple wells to reduce the time frame necessary to obtain ZVI-impacted groundwater samples by inducing a steeper groundwater gradient between the ZVI panels and performance monitor wells to attempt to increase the in situ remediation was implemented as a result of continuously optimizing performance when possible.

Summary of Results
Contractor installed the ZVI emplacement system over an area approximately 45 feet long and 45 feet wide, between approximately 55 and 75 ft bls. Wellhead pressure and electrical resistance tomography were monitored to track installation of the panels. Construction of the ZVI emplacement system commenced on September 15, 2014, and was completed on September 30, 2014. The ZVI multi-azimuth grid installed in the TFC hotspot source area included the following materials and processes:

- nine emplacement boreholes with two 5-foot expansion casings (that is, upper and lower) installed to a depth of approximately 75 ft bgs using the mud-rotary drilling technique
- seven resistivity strings with five receivers each, for a total of 35 receivers installed to a depth of approximately 75 ft bgs using a direct push drilling rig
- injection of 21 tons of granular ZVI, about 33% in the upper zone and 67% in the lower zone, and application of a total of approximately 5,820 gallons of inclusion fluid during the emplacement process

Video-logging and redevelopment of area wells following ZVI emplacement indicate that there were no adverse impacts to existing wells as a result of the implementation process. Postimplementation sampling for VOC analysis, dechlorination daughter products, metals, and general minerals began in November 2014 and continued in 2018. Groundwater field parameter measurements, including dissolved oxygen, specific conductance, ORP, pH, and temperature, also continued in 2018.

E-6. Oxidant Surface Eruption During Direct Push Injection

Location
Anonymous

Reference Material
Internal distribution only

Regulatory Phase
None reported

Amendment(s)
Sodium permanganate

Remedial Technology
Subsurface injection

Site Description and Approach

Direct Push Injection

Optimization/Lessons Learned
Direct push equipment was used to inject sodium permanganate into a shallow groundwater system at a U.S. Air Force base in California. The site soils were compactable and had low to moderate hydraulic conductivity. Oxidant flow rates were near zero at low injection pressure and the contractor increased pressures until reagent delivery rates increased. As a result, eruptions of the oxidant occurred at the ground surface. Postinjection sampling showed that nearly all the reagent missed its intended target zone in the groundwater, accumulating instead in the overlying unsaturated zone.

Summary of Results
None available

E-7. TerraVac Under EPA's Demonstration Program Conducted SVE in the Source Area

Location
Groveland, Massachusetts

Reference Material
Draft Final Source Area Re-evaluation Report Groveland Wells Nos. 1 & 2 Superfund Site 2006

Contaminant
Aqueous and NAPL trichloroethylene (TCE)

Regulatory Phase
SVE was ineffective and ISCO was subsequently demonstrated. No source control, but further investigation led them to treat the source.

Amendment(s)
Potassium permanganate

Remedial Technology
Insitu chemical oxidation

Site Description and Approach

At the conclusion of the ex situ test, an in situ soil mixing and chemical oxidation test was performed. A treatment area of approximately 470 square feet was divided into a grid with eight cells. Soil was excavated to around 5 feet. Potassium permanganate was used to treat 90 cubic yards of shallow soil. The excavated soil was treated with potassium permanganate and mixed with water in the excavation using an excavator. Each grid did achieve some remediation, but not completely. In some cases, the post-treatment samples had higher concentrations of TCE than the pre-treatment samples (that were taken from the same area).

Optimization/Lessons Learned
Between 2004 and 2006, EPA performed a comprehensive source area investigation, underground storage tank (UST) removals, and chemical oxidation treatment pilot studies that were documented in the Source Area Re-evaluation Report. The report concluded that the initial SVE remedial action had been largely ineffective and that significant source area contamination remained (soils contaminated with TCE up to 52,000 ppb). Groundwater in the source area had TCE contamination as high as 160,000 ppb.

Summary of Results
Costs were compared for in situ chemical oxidation for both saturated and unsaturated soils and using ERH for both. The conclusion was that chemical oxidation would cost about $2 million more than ERH and would be conducted over 5 years, whereas ERH would take about 1 year. EPA chose ERH over chemical oxidation for the site based on the results of the Source Area Re-evaluation, including cost estimates for various remedial options. In 2007, EPA issued an Explanation of Significant

Differences (ESD) for the source control remedy modifying it to include ISTT along with SVE to address soil and groundwater contamination remaining on the Valley Manufacturing property within the source area. [“Final Remedial Action Report, Groveland Wells Numbers 1 and 2 Superfund Site – Operable Unit 2.” Noblis Engineering, Inc., September 20, 2011, page 6, unavailable.]

E-8. Unusual Dichloroethylene Isomerizations and External Nitrate Input to Help Decipher in Situ Pilot Test Outcomes

Location
Urban Gulf Coast, Florida

Reference Material
Importance of Unusual Dichloroethylene Isomer and Sewer Leakage to an In situ Remediation: Studer, J., 2017. 17th International Contaminant Site Remediation Conference, September 10-14, Melbourne

Contaminant
VOCs

Regulatory Phase
This pilot study represents an interesting example where outcomes from a field pilot test of an in situ groundwater treatment technology strayed significantly from expectations.

Amendment(s)
None reported

Remedial Technology
Biogeochemical Reductive Dechlorination

Site Description and Approach

Site Description:
Shallow and deep weathered limestone bedrock zones at a depth of 40 meters.

Approach:
The pilot goal was to test biogeochemical reductive dechlorination (BiRD) to accelerate remediation. 7,425 liters of reagent solution was pressure-injected into each zone.

Optimization/Lessons Learned
In depth analysis identified rapidly rising nitrate concentrations and high trans-1,2 DCE to cis-1,2 DCE ratios as two quite unusual site features that led to the conclusions that

- injectate emplacement was highly preferential to the detriment of treatment at the central monitoring wells
- in situ biogenic ferrous sulfide production with complete dechlorination treatment did occur in the limestone but native partial dechlorination of TCE was also stimulated
- nitrate originating from a previously unknown overlying sewer leak was preventing the shallow zone near the central monitoring well from transitioning into deep reducing conditions necessary for sulfate reduction, a prerequisite to BiRD

Summary of Results
The pilot test involved a shallow injection zone and a deeper injection zone within a variably weathered limestone harboring a TCE and DCE groundwater plume. Natural biodegradation was slowly degrading the TCE to DCE but mineralization was not apparent. A bench treatability study demonstrated in situ biogenic ferrous sulfide production and TCE and DCE transformation without VC production. A reagent formulation identified from the bench study was the basis for 7,425 liters of reagent solution pressure-injected into each zone. The central monitoring well in the shallow zone did not respond to injection even after 9 months. The central monitoring well in the deep zone did not immediately respond but eventually injectate components were detected due primarily to diffusion and TCE and DCE concentrations declined without VC production. This was perplexing given that the central monitoring well screens were only 4.6 meters from multiple injection well screens. Further explanation of the site in the Clu-IN 2017 reference states that unsuspected sewer leakage introduced nitrogen to the alluvium, resulting in maximum detected NO_3 of 120 mg/L in shallow bedrock. Following discovery and repair

of the sewer break, in depth analysis aided by bench study insights suggested that BiRD can be a good match for the bedrock if an improved reagent distribution process is implemented allowing transition into deep reducing conditions necessary for sulfate reduction, as BiRD requires.

E-9. In Situ Bioremediation and Soil Vapor Extraction at the Former Beaches Laundry & Cleaners

Location
Jacksonville Beach, Florida

Reference Material
In situ Bioremediation and Soil Vapor Extraction at the Former Beaches Laundry and Cleaners

Contaminants
PCE, TCE, cis-1,2 DCE, and VC

Regulatory Phase
Florida RCRA process

Amendment(s)
Potassium lactate and denatured alcohol

Remedial Technology
Excavation, co-solvent flushing, and enhanced bioremediation with source control

Site Description and Approach

Site Description:
The soil profile at the site consists of silty, fine to very fine-grained sand with shell fragments from surface to 40–50 feet bgs. Underlying the surficial sands is approximately 3 feet of clayey sand followed by 12–15 feet of clay overlying clayey sand. The maximum depth evaluated in the site investigation was 65 feet bgs. The shell fragments and carbonate sand grains found in the subsurface increased the buffering capacity of the soil. There are three groundwater zones at the site: shallow, intermediate, and deep.

Approach:
Three pilot injections of Fenton’s reagent (hydrogen peroxide and ferrous iron catalyst) were conducted from July 1999 to August 2000 and did not significantly reduce VOC concentrations in groundwater. Therefore, a revised remedial action plan consisting of a phased approach was implemented. The phased approach included excavation of contaminated soil followed by use of the SVE system to accelerate the removal of mass from the source area. A total of 244 tons of contaminated soil was excavated from the northeast corner of the Beaches building. Following soil excavation, the SVE system began operation on February 7, 2007 to address remaining soil contamination in the vadose zone of the site. Florida Department of Environmental Protection approved the soil excavation work plan, which recommended placing 11 horizontal SVE wells in the excavated area to allow subsequent treatment of soil containing less than 17 mg/kg of PCE to be left in place near building bearing walls.

Groundwater treatment consisted of in situ enhanced bioremediation to expedite the bioremediation process of the plume through the addition of nutrient amendments (potassium lactate and denatured ethanol). Implementation of the final 2006 remedial action plan for the enhanced bioremediation injection system was initiated by constructing six new injection wells spaced approximately 12 feet apart along the northern and eastern edges of the northeast corner of the building; each well contained screened injection points at three different depths. The 2006 remedial action plan also specified the use of three existing monitoring wells as additional injection points and the use of the 11 SVE wells as surface-level injection points. A total of 21 vertical injection points were used, including seven well points between 10 and 20 feet bgs, seven at 20–30 feet bgs, and seven at 30–45 feet bgs. In addition the 11 SVE wells were used to inject into the first 3 feet of soil. Only five of the 11 SVE wells were used during the first and third injections, and the other six wells were used during the second and fourth events. All of the 11 SVE wells were used during the fifth and sixth events. During the enhanced bioremediation, January to June 2008, a total of 77,400 gallons of potassium lactate and ethanol solution was injected into the groundwater and flushed with 10,800 gallons of water over a 6-month period, at depths ranging from 2 to 45 feet. In 2009 the SVE system was shut off.

Optimization/Lessons Learned

Baseline and postinjection monitoring was conducted at the site for both the SVE and enhanced bioremediation system. The goals of the revised remedial action plan were to reduce PCE, TCE, cis-1, 2 DCE, and VC contaminant concentrations in the soil to below Florida State Cleanup Target Levels, and to reduce the groundwater contaminant concentrations to below the Florida Natural Attenuation Default Criteria (FNADCs). Once the FNADC were achieved, it is anticipated that natural attenuation will reduce the contaminant concentrations to below FSCTLs. Samples collected from the influent of the SVE system indicated that PCE and methane concentrations were below the detection limit; therefore, the SVE system was shut down and converted to a passive system in March 2009. Groundwater concentrations of PCE and TCE continued to exceed the FNADCs at several locations within the aquifer based on sampling in July 2008. Analytical results indicate that the phased remedial action at the site resulted in significant reductions in contaminant concentrations that were continuing to decrease.

Summary of Results

Soil excavation: The source removal goal of removing all materials with PCE concentrations above 17 mg/kg was accomplished in the southern and western portions of excavation.

Soilvapor extraction: The SVE vapor influent concentrations were successfully reduced to below the detection limits. The SVE system was shut down during the injection and the SVE lateral wells were used for injection wells.

Enhanced bioremediation: To decrease costs, the existing SVE, injection and monitoring wells were used to inject the amendment. Ball valves were installed on the SVE wells to prevent the amendment slurry from entering the SVE system piping inside the trailer. Based on the analytical results from the first four injections, the remedial action plan was modified to increase the amount of potassium lactate used in the injection. In addition, the injected volume was increased by an additional 300 gallons of water per well to distribute more carbon from the amendment in the intermediate and deep zones of the aquifer. Increasing the mass of electron donor in the bioremediation injection system increases the production of methane. The SVE system will provide the engineering control to address excessive methane generation. The potassium lactate and denatured ethanol amendments were effective in accelerating the biodegradation of PCE and PCE degradation products. The total VOC reduction ranged from 65 to 99% in the shallow zone wells. More targeted injections for the intermediate and deeper levels are needed to enhance the reductive dechlorination at the site. The addition of vertical injection wells upgradient of the site helped further enhance the capability to deliver electron donor to source areas with elevated VOC concentrations. Use of existing horizontal SVE wells for the bioremediation injections helped lower the cost to implement the series of injections.

E-10. LNAPL Remediation Combining Mobile Dual Phase Extraction with Concurrent Injection of a Carbon-Based Amendment: Little Mountain Test Facility

Location

Hill Air Force Base, Utah

Reference Material

Site WR111 Little Mountain Test Facility Final Status Report Draft Final 2018

Contaminant

Aqueous and NAPL benzene and trimethylbenzene compounds (1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene)

Regulatory Phase

Chemically oxidized granular activated carbon (COGAC) was selected for injection based on results of a bench-scale treatability test. This amendment uses ISCO, biostimulation, and carbon adsorption.

Amendment(s)

Chemically oxidized granular activated carbon (COGAC)

Remedial Technology

Mobile dual phase extraction (DPE) and ISCO with biostimulation. Combined aggressive petroleum mass removal (free product and dissolved phase) by mobile dual phase extraction with concurrent injection of carbon combined with chemical oxidants and oxygen-generating compounds to promote natural attenuation of residually entrapped mass.

Site Description and Approach

Site Description:
Silty fine to medium sand, silty clay, and clay. Groundwater is approximately 17 ft bgs. From lower to upper in the stratigraphic sequence: slate, greenstone, and tillite.

Approach:
Over this 1-acre site, 48 extraction points were installed with 118 surrounding injection points in a systematic grid fashion. The temporary injection points were advanced with a 2.25-inch DPT rod. The goal of this project was to transition from initial chemical oxidation to longer term aerobic bacterial growth combined with carbon adsorption. ISCO uses sodium persulfate catalyzed by calcium peroxide to produce persulfate radicals with the ability to oxidize contaminants for days or weeks. Biostimulation is promoted by residual nutrients from the ISCO activity and the degradation of calcium peroxide into hydrogen peroxide, which provides the groundwater with elevated dissolved oxygen to enhance aerobic biological activity. The activated carbon itself provides both adsorption sites for organic contaminants to minimize desorption rebound as well as a substrate for the growth of contaminant-degrading bacteria. A 12% COGAC solution was prepared in a large mixing truck and pumped directly into each injection point. COGAC was injected using a bottom-up procedure. Concurrently, groundwater and LNAPL were extracted through 1-inch schedule 40 PVC pipe. A vacuum trailer was used to remove groundwater and LNAPL, and the extracted water was stored in a frac tank for later disposal. The mobile DPE was conducted concurrently with injection, just beyond the typical ROI. Over 15 pounds of amendment (for each pound of contaminant mass) was injected and evenly distributed throughout the treatment area. The placement of injection and extraction points was designed and field-adjusted to achieve hydraulic capture and control.

Optimization/Lessons Learned
Amendment distribution was vastly improved by combining mobile DPE vacuum (at extraction points) with amendment injection (at nearby injection points), thereby increasing sweep efficiency of amendment delivery through promotion of enhanced pressure gradients. Visual observations, collection of cores at injection points, and daily monitoring of the location, movement, and thickness of LNAPL were completed. . Results presented will elaborate on these findings as well as other performance metrics.

Summary of Results
Concurrent implementation of mobile DPE and injection of COGAC resulted in effective distribution of the amendment throughout the smear zone area and near-complete elimination of measurable free phase LNAPL. Initial post-treatment study data indicate decreasing trends in dissolved phase benzene and benzene compounds.

E-11. Eastern Surplus Company Superfund Site, Southern Plume: Meddybemps

Location
Washington County, Maine

Reference Material
[Examples of Groundwater Remediation NPL Sites, USEPA 542-R-18-002]()

Contaminants
Chlorinated VOCs including PCE and TCE, metals including manganese and lead, and PCBs; highest concentrations in groundwater included 6,700 ppb PCE (northern plume) and 1,100 ppb PCE (southern plume). NAPL suspected in northern plume.

Regulatory Phase
Post-ROD, 5-year review, ESD. Bench-scale and pilot study worked in southern plume but northern plume concentrations increased. As part of ESD, bench- and pilot-scale tests changing from in situ chemical oxidation to enhanced in situ bioremediation.

Amendment(s)
Enhanced in situ bioremediation

Remedial Technology
Soil excavation and waste removal, pump and treat, ISCO with sodium permanganate injections, with most recent in situ

bioremediation.

Site Description and Approach

Site Description:
Overburden consisting of stratified beds of gravel, sand, and mixed sands and silt, and shallow bedrock. There are two distinct plumes, northern representative of conditions post-EISB is in bedrock, while the southern plume migrated underneath the southern area of the site in overburden and shallow bedrock.

Approach:
The Record of Decision includes pump-and-treat systems for northern and southern plumes with ISCO, which worked primarily in the southern plume but not efficiently in the northern plume. In 2010, EPA with the concurrence of MEDEP shut down the southern extraction system and in 2011 under MEDEP the southern system was decommissioned.

With PCE and TCE concentrations remaining elevated in the northern plume, EPA and MEDEP agreed to conduct a bench-scale test to assess the applicability of bioremediation as a viable alternative to ISCO. Based on applications at other sites, EISB offered extended residence time for the injection material and improved degradation of the residual VOCs present in the bedrock fractures and rock matrix. In 2011, site groundwater and rock matrix material from a newly installed well were used to run a 49-day bench-scale test. The bench test results suggested that complete dechlorination from PCE to ethene could be achieved using site groundwater, an electron donor (for example, vegetable oil), a proprietary culture of *Dehalococcoides* (Dhc), organic soluble substrate (lactate), and mineral amendments.

After implementation of the bench-scale then pilot-scale investigation of EISB, EPA issued the ESD to change the in situ oxidation treatment to an in situ bioremediation treatment, leading both agencies to agree to a pilot-scale implementation. The operation of the northern extraction system was suspended, and four wells were used to inject EISB mixture. The pilot test consisted of two application events within the approximately 50-foot-diameter target area. During each application, groundwater from four pilot test area wells was extracted, stored in aboveground tanks, mixed with mineral amendments and Dhc bacteria, and then reinjected. Finalization of the ESD has led to the implementation of a source control full-scale bioremediation effort. The design for the full-scale effort was completed in September 2018 and mobilization for the full-scale implementation was expected to occur in November 2018.

Optimization/Lessons Learned
The southern contaminated groundwater plume was successfully treated using a conventional pump-and-treat system supplemented by the injection of sodium permanganate (ISCO) to accelerate degradation of contaminants. As a result of this approach, combined with source removal during the Non-Time-Critical Removal Action, the approximately 1.5-acre southern plume was cleaned up to drinking water standards, and extraction wells located within the southern plume were shut down in late 2010. Remediation continues, however, within the northern plume, where concentrations are still above MCLs due to the more complex geology and higher (DNAPL range) initial concentrations in groundwater.

Summary of Results
PCE concentrations in 1.5-acre southern plume reduced from 1,100 ppb to below cleanup level. Chlorinated VOC concentrations in northern plume are still above cleanup levels. Current site use includes a major archaeological research site for the history of the Passamaquoddy people.

E-12. Hollingsworth Solderless

Location
Fort Lauderdale, Florida

Reference Material
Examples of Groundwater Remediation NPL Sites, USEPA 542-R-18-002

Contaminants
Chlorinated VOCs including TCE, cis1, 2-DCE, and vinyl chloride in groundwater; TCE in soil; highest concentrations in groundwater included 4,300 ppb TCE, 10,000 ppb cis-1, 2-DCE, and 6,000 ppb vinyl chloride.

Regulatory Phase
Post-ROD and ESD, using ROD amendment for in situ ERD. Pilot study followed by additional injections result in ROD amendment.

Amendment(s)
Potassium lactate and DHE bacteria

Remedial Technology
Soil excavation and off-site disposal, groundwater pump and treat with air stripping, SVE, in situ ERD with potassium lactate and bacteria injections

Site Description and Approach

Site Description:
Site overlies Biscayne aquifer, which is highly permeable, unconfined, and composed of a fine- to medium-grained sand, sandstone, and limestone sequence.

Approach:
The cleanup approach in the ROD included excavation, ex situ aeration, and replacement of soil in the area of excavation. The ROD also specified extraction, treatment with air stripping technology, and reinjection of groundwater into the aquifer. Due to water levels reaching historically highs in the late 1980s, the soil excavation and replacement were changed to in situ SVE operated from January 1991 to July 1991, when the soil cleanup level of TCE concentrations less than 1 ppm was achieved. The groundwater treatment system ran from 1992 to 1994, when the system was removed because it was ineffective. However, groundwater rebound resulted in a 2001 ESD for additional soil removal in two distinct areas (south and west drain field areas). Groundwater monitoring showed decreased VOCs in the shallow groundwater but no similar decline in deeper groundwater. A pilot study was initiated for south and west drain fields from 2005 to 2007 using potassium lactate injections and bioaugmentation. The study demonstrated success in reducing VOC concentrations. A 2008 ROD amendment was completed for a site remedy of in situ ERD with potassium lactate injections.

Optimization/Lessons Learned
The initial groundwater remedy removed up to 55 pounds of contaminants each day. Over 300 tons of contaminated soils were removed. Chlorinated VOC concentrations in groundwater were reduced up to 98% in just over 2 years using ERD. Vinyl chloride is the only remaining groundwater contaminant detected above cleanup levels.

Summary of Results
The combination of excavation/removal and pump and treat was also used frequently at the sites that achieved significant progress toward groundwater restoration presented in the USEPA report Examples of Groundwater Remediation at NPL Sites, May 2018. At the Hollingsworth Solderless site, it was determined that a pump-and-treat system was no longer effective at decreasing concentrations of TCE, cis-1, 2-DCE, and vinyl chloride after 2 years of operation. After a successful pilot test of in situ bioremediation, an ROD amendment was issued in 2008 modifying the site remedy from pump and treat to in situ bioremediation (that is, enhanced reductive dechlorination).

E-13. Former Industrial Site Characterization and Remediation in Fractured Rock

Location
Greenville, South Carolina

Reference Material
Characterization and Remediation in Fractured Rocks

Contaminants
TCE; cis-1, 2-dichloroethene; vinyl chloride

Regulatory Phase
Pilot test and full scale

Amendment(s)
ZVI and potassium permanganate

Remedial Technology
Permanganate solid slurry injection for ISCO in source area. ZVI solid slurry injection for ISCR in plume area.

Site Description and Approach

Site Description:
The site is underlain by saprolite that grades into competent bedrock. The saprolite is heavily oxidized, relatively low permeability silt, sand, and clay, with varying degrees of relict bedrock structures and quartz veining. The transition from saprolite to competent rock is a partially weathered rock zone that is visually similar to the saprolite but marked by greater density and more abundant rock fragments. The upper bedrock exhibits varying degrees of fracturing and weathered zones in a matrix of mica schist and gneiss, feldspar gneiss, and granite. The depth to rock ranges from approximately 90 feet bgs in the source area to as shallow as 6 feet in the plume area.

Approach:
Since investigations began in 1996, site characterization has been conducted in multiple phases and has used traditional monitoring wells and a range of additional tools.

Field pilot tests of ZVI in the plume area and permanganate in the source area were conducted in 2011. Borings were advanced immediately after the injection to assess physical reagent distribution, and groundwater was monitored for 2 years following the pilot. Based upon the pilot test results, a full-scale design was implemented in 2013. A total of 83 tons of potassium permanganate blended with sand was injected via 87 discrete vertical intervals in 14 injection wells over the course of the pilot- and full-scale ISCO remedial action. A total of 725 tons of ZVI was injected via 368 discrete vertical intervals in 62 injection wells in three barriers across the plume, over the course of the pilot- and full-scale ZVI remedial action. The full-scale remedial actions were conducted from July 2013 to July 2014. An additional 5,208 gallons of 5.3% sodium permanganate solution was injected by gravity feed at two well locations in September 2015 to address a small portion of the site that was not effectively treated during the full-scale injection.

Direct push and hand-auger soil sampling was conducted where possible to delineate shallow soil. Traditional hollow-stem auger drilling was used in the saprolite. Air, mud rotary, and core drilling were used in the bedrock. FLUTe liner was used for DNAPL screening. Discrete-interval sampling tools, passive diffusion bags, and HydraSleeve samplers were used primarily to provide vertical delineation in the source area. Passive diffusion bags were also used for an in-stream assessment. Summa canisters and Dräger tubes were deployed for indoor air and soil vapor characterization. Screening-level grab groundwater samples were collected during sonic drilling of wells for reagent injection using the Isoflow discrete-interval sampling system developed by Boart Longyear. The overall remedial evaluation, implementation, modification, and performance assessment for the remedial actions since 2011 (the permanganate ISCO and ZVI remedial actions) were developed based upon guidance in the Integrated DNAPL Site Strategy document (2011c). Remedial evaluation began with an assessment of remedial objectives. The absolute objective was to restore the overburden and bedrock aquifer to drinking water standards.

Optimization/Lessons Learned

Pilot test results were used to optimize the full-scale remedial design. Procedures were developed to assess field observations and results daily to continuously refine the site conceptual model and to optimize the design to match site conditions during construction. Ongoing remedy performance and progress toward (or achievement of) the functional and absolute objectives are evaluated with an extensive groundwater monitoring program. Additional injections have been conducted based upon the results to address small areas exhibiting rebound and requiring further treatment. The large plume area, limited plume access, concentrated source area, and dual-zone (saprolite/bedrock) aquifer system pose special challenges. Remedial designs and objectives are often based on differentiation between overburden and bedrock with little consideration of the transition zone between these regions. A valuable lesson learned at this site was the importance of the partially weathered rock transition zone between saprolite and bedrock. This zone exhibits significant vertical and lateral variability and has a hydraulic conductivity that averages about one order of magnitude higher than the saprolite. The variability required ongoing assessment and remedial design modification during construction.

Summary of Results

Results to date have generally met expectations based upon the REMChlor and PREMChlor modeling predictions with respect to source and plume concentration reductions. A few locations in the source area have required additional injection to address rebound, and plume-area monitoring wells located distally from the ZVI barriers have not yet exhibited reductions because sufficient time (relative to transport velocity) has not passed. Permanganate breakthrough from the source area to one boring location in the closest ZVI barrier has been observed in the latest sampling events. The baseline represents the condition prior to the 2011 pilot test. Overall groundwater TCE concentrations (through January 2016) have been reduced by >99.9% in 12 of 15 monitoring wells, and by 99.4%, 99.0%, and 73.8% in the remaining three wells. The poorest performance (73.8% reduction) is in a well located within the former tank excavation and reflects rebound following >99.9%

removal immediately after the remedial action. Additional sodium permanganate injection is planned for this location. The core of the plume (10,000 mg/L to a maximum of 96,000 mg/L TCE) has contracted significantly, with remaining TCE concentrations <2,230 mg/L. Results for MW-33, the plume monitoring well exhibiting the highest baseline TCE concentration, have been reduced by 99.2% from a maximum of 110,000 mg/L one week after the field pilot test in May 2011 to 905 mg/L in the latest sampling event (January 2016) (Figure11-3). The concentration of cis-1, 2-dichloroethene (formed as an intermediate degradation product from TCE) exhibited initial increases from the baseline (<2,000 mg/L) to a maximum of 43,000 mg/L, and has subsequently degraded to 1,650 mg/L.

E-14. Naval Submarine Base Kings Bay, Site 11

Location
Camden County, Georgia

Reference Material
Naval Submarine Base Kings Bay Site 11

Contaminants
Aqueous PCE, TCE, DCE, and vinyl chloride

Regulatory Phase
Georgia Environmental Protection Division RCRA corrective action

Amendment(s)
Fenton’s reagent

Remedial Technology
Pump and treat (P&T), ISCO (Fenton’s reagent), biostimulation, monitored natural attenuation (MNA). No source control included.

Site Description and Approach

Site Description:
Marginal marine sediments of barrier island and back-barrier lagoon origin. Permeable sand underlying the site exists between 32 and 42 ft bgs and is underlain and overlain by finer grained sand and clay of back-barrier lagoon origin, characterized by lower hydraulic conductivity. A layer of organic-rich sand overlies the aquifer.

Approach:
In November 1998, two extraction wells and six process monitoring wells were installed along with 23 specially designed injection wells that were placed in and around the source area. The monitoring wells were sampled twice each day and analyzed for pH, specific conductance, alkalinity, iron, sulfate, sulfide, dissolved hydrogen, and dissolved oxygen, as well as any change in contaminant concentrations. The modified Fenton’s reagent containing 50% hydrogen peroxide was injected in two phases. Phase 1 of the ISCO treatment focused on the central part of the contaminant plume, while phase 2 focused on the downgradient areas that were not treated during phase 1.

The modified Fenton’s reagent containing 50% hydrogen peroxide was injected in two phases. Phase 1 of the ISCO treatment focused on the central part of the contaminant plume, while phase 2 focused on the downgradient areas that were not treated during phase 1. Following phase 2, during which 21 new injectors were added, elevated contaminant concentrations (1,700 µg/L) were detected outside the plume near one of the injectors used during phase 1, indicating the presence of a previously unidentified contamination source area. Thus, two more phases were added to the treatment process. The last treatment phase was administered in November 2001.

Optimization/Lessons Learned
Because adding Fenton’s reagent to an aquifer can change both the geochemistry and the microbial population, monitoring was performed. Measurements in one monitoring well showed an increase in dissolved oxygen from nondetect before injection to > 7 mg/L after injection. Also, microbial activity decreased after each injection. Dissolved hydrogen concentrations indicated that the injection of the ferrous iron activator had shifted the microbial activity from sulfate- and iron-reducing to a more purely iron-reducing environment. To reverse this trend, a solution of emulsified vegetable oil (35% soybean oil with lecithin and 65% water) was injected into the aquifer after phases 3 and 4 to return the subsurface environment to an anaerobic state and potentially restore some of the sulfate-reducing activity that increases PCE and TCE

degradation. Microbial activity generally rebounded within a few months of each Fenton's reagent injection.

Summary of Results

In all, about 48,000 gallons of 50% hydrogen peroxide solution and a similar volume of ferrous sulfate catalyst were injected into the aquifer—principally in the more permeable zone between 32 and 42 ft bgs. In addition, about 25,000 gallons of the emulsified vegetable oil solution were injected following Fenton's reagent application phases 3 and 4. The plume size shrank by about 70%. Levels of total chlorinated hydrocarbons in the most contaminated area decreased from nearly 200,000 µg/L in 1999 to 120 µg/L in 2002. Currently, chlorinated hydrocarbon levels range from <1 to 13.9 µg/L. As of May 2003, no additional exceedances of MCLs occurred in any of the off-site monitoring wells, and many of the on-site monitoring wells had no measurable levels of contaminants. As a result, the P&T system was shut off 2 months after the phase 2 ISCO treatments, and MNA has been implemented as the final corrective action for the landfill. There was no need for further treatment with UV oxidation. Shutting down the P&T system slowed the transport rate of contaminants downgradient, which increased the effectiveness of the biodegradation process.

Since 1999, two long-term monitoring programs have been conducted at Site 11, including monitoring as required by the RCRA permit and performed in accordance with the associated Groundwater Monitoring Plan (GWMP) (Bechtel 1999), and monitoring conducted by the United States Geological Survey (USGS) in coordination with the Navy to evaluate the effectiveness of natural attenuation processes in reducing contaminant concentrations (USGS 2009). The RCRA permit required that monitoring begin in 1999, and the monitoring program was adjusted several times based on the exit strategy provided in the GWMP and other recommendations from the Georgia Environmental Protection Division. The USGS monitoring was conducted from 1999 to 2009 at a number of designated wells. The study confirmed the effectiveness of natural attenuation processes at Site 11 (USGS 2009). After the completion of the USGS study, these USGS monitoring wells were not sampled in 2010. Groundwater was sampled in 2011, and a new sentinel well was installed in 2012. Optimization reports have been performed, and the site is currently under a monitored natural attenuation phase.

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Appendix F. Performance Evaluation & Optimization of In situ Remediation using Amendment Delivery

This checklist is meant to assist the optimization team in evaluating the overall performance of an in situ remediation system for removing contaminants from groundwater and soil. It is intended for use in the implementation and feedback/monitoring phase for the evaluation of full-scale implementation or pilot testing. The checklist is divided into the following sections:

1. Evaluation team composition
2. Typical treatment objectives
3. References
4. Data collection requirements
5. Performance analysis
6. Alternatives for performance improvement and possible cost savings
7. Supplemental notes and data

The checklist provides suggestions for information gathering and possible project recommendations. Space has been provided to record data and notes from the site visit. Supplementary notes, if required, should be numbered to correspond to the appropriate checklist sections.

Typical Performance Problems

A number of general performance problems commonly occur at sites where amendment injection is attempted.

- The amendments are not adequately distributed so reactions of the amendments with the contaminants are not occurring. An inadequate density of injection points, unrecognized subsurface heterogeneity, or inadequate persistence of amendments may prevent proper distribution of amendments throughout the target zone. This includes inadvertent injection of amendments intended for the saturated zone into the vadose zone and excessive daylighting.
- The amendments are not delivered at an adequate dose or volume to support and sustain the desired decrease in contaminant concentrations. The degradation of contaminants may not proceed to desired (innocuous) end products or unexpectedly large rebounds in concentrations may occur.
- The chosen amendments are not effective at creating conditions necessary for degradation/destruction of all of the contaminants to innocuous end products. This could include the previously unrecognized need for activation of a specific oxidant (for example, persulfate) or for bioaugmentation for successful bioremediation. The chosen amendments may not persist adequately to be delivered to the target treatment volume or to address rebound due to diffusion from low permeability zones.
- The monitoring of the subsurface conditions and delivery process is inadequate to assess success. This may include spatial, temporal, and analytical limitations in the monitoring program. This may also include use of inappropriate sampling methods to assess performance. Operational data such as volumes, pressures, etc., may not be recorded or may be recorded only in field forms or log books and subject to more errors than electronic records.

The questions below are meant to help determine if these problems have occurred at the site. Recommendations to address these conditions to improve performance (and to reduce cost) are presented in a following section.

1) Evaluation Team Composition

The following disciplines would typically be included in the evaluation team for an in situ amendment injection system:

- Hydrogeologist
- Environmental, civil, or chemical engineer with relevant experience
- Environmental scientist

- Regulatory specialist

2) Typical Treatment Objectives

In situ amendment injection is typically done to alter geochemical conditions to destroy and/or immobilize contaminants in the saturated zone and occasionally in the vadose zone. Clean up goals may include the reduction of contaminant concentrations to below some standard or threshold throughout the source area, plume, or downgradient of an injection line/trench.

Verify that the treatment objectives, established for when the in situ remediation project was designed and implemented, are SMART (specific, measurable, attainable, relevant, and timely).

3) References

See references provided in the ITRC Optimizing Injection Strategies and In situ Remediation Performance Technical Regulatory Guidance**.**

4) Data Collection Requirements

It is recommended that the following information be collected on a scheduled basis and routinely evaluated to assess the performance of the in situ treatment system. Record the appropriate units with each value.

a) Describe the objectives for the amendment injection. These may be general *(for example, reduce groundwater contaminant concentrations; reduce mass flux to allow natural attenuation to be effective; alleviate vapor intrusion, etc.),* but should be SMART (*for example, attain a specific amendment concentration at certain monitoring points within a specific time; achieve a certain zone of influence as measured by specific parameters*). If current objectives are poorly defined or not defined at all, describe what might be reasonable objectives given information from the owner and regulator.

b) What is the estimated time frame for injection operations and attainment of objectives? What is the basis for this estimate? What statistical methods will be employed to evaluate whether or not remediation is on track?

c) Obtain/display available hydrogeologic information, with specific emphasis on the degree and complexity of heterogeneity in the TTZ. This would include detailed geologic cross-sections. Summarize the hydrogeologic factors, including high permeability layers or lenses, bedrock valleys, and higher transmissivity weathered rock that would affect the delivery and transport of the amendment.

d) What is/was the three-dimensional TTZ? Describe (or attach map and cross-sections).

e) Access maps of the injection locations and describe the injection strategy (for example, whether the injection is done via wells or temporary points; injection barrier or grid; recurring injections).

f) Gather the performance monitoring data, including:

- concentrations trend analysis and raw concentration data of contaminants in all media and potential treatment byproducts
- applicable geochemical and, if applicable, biological data
- concentrations of amendments (or tracers) in monitoring wells
- recent injection volumes, pressures, depths, and concentrations
- piezometric levels for the aquifer, if applicable

g) Describe the performance monitoring network, including source area wells, sentinel wells, plume migration wells, and point of compliance wells. Determine what vertical intervals the wells monitor relative to the target treatment intervals. Describe how these wells will be monitored (for example, low flow sampling, passive diffusion bags, in situ monitoring data loggers, etc.) and for what parameters?

5) Performance Analysis

a) Performance monitoring data:

Are the correct media and vertical interval being monitored/sampled? Link (Section 4.4.2)

Are the monitoring locations and vertical intervals adequate to allow reliable data to be collected regarding injection distribution and concentration reduction? Link (Section 4.4.2)

Are the constituents of concern (CoCs) and all potential byproducts being monitored?

What other parameters represent “lines of evidence” to support the attainment of remedial or treatment goals for the site in question?

Is the current level of data collection sufficient to enable the performance metrics to be reliably and conclusively analyzed?

b) Subsurface amendment distribution

Was there adequate evidence the amendment was distributed laterally and vertically to address the TTZ (for example, based on amendment concentrations, tracers, or other indirect indicators of the presence of amendments)? _______ If not, indicate the areas on a map and/or cross-section.

If advective and dispersive transport of amendments was anticipated to distribute the amendment, did the arrival of the amendment roughly coincide with the time expected and at the concentration expected? _______

Is the distribution of amendment and/or effects on contaminant concentrations consistent with the CSM (that is, are there unexpected flow directions or preferred pathways)? _______

If the amendments are intended to persist at concentrations needed to promote on-going degradation and address diffusion limitations, are the declines in amendment concentrations consistent with expectations? _______ If not, what is the likely cause (for example, higher than expected groundwater velocities; more rapid reactions than anticipated)?

Was there evidence that injection of amendments displaced contaminants outside of the target zone into other areas at unacceptable concentrations? ______

c) Injection/Amendment Delivery

Were injected volumes smaller than planned at some points (for example, due to low permeability, surfacing, inadequate supply)?

Were there any leaks/spills of the amendments that were not appropriately cleaned up/addressed? _______

Were there excessive occurrences of daylighting? _______ If yes, where did it occur (for example, by the injection point or away from the borehole)?

Were the appropriate amendments added at the appropriate dosage/concentrations, based on the available records? _____

Was the rate at which injection occurred slower than planned? _______

Were injection pressures higher than expected or did they spike to a value greater than the overburden pressure such that fracturing is likely? _______

Were the injection flow rates substantially greater than or less than expected based on the design or pilot testing (indicate which condition occurred)? ______

Is there evidence that any permanent/temporary injection wells have experienced decreased injection capacity due to scaling or biofouling? ______

Can the injection depths be verified and were they at planned intervals or intervals appropriate based on data collected during the remedy implementation? _______

Was there evidence of amendment loss to the vadose zone, such as daylighting, infiltration to vapor wells, injection into points with screen or fractures above the water table, or ground displacement monitoring (if the saturated zone was the target)? _______

Were the injection points/wells placed as close as practical to the intended locations shown in the plans? _______

Was anisotropy observed as a major issue that would affect adequate distribution, based on information generated during site characterization (for example, pumping test response, observed fracture orientation, hydrogeologic setting)? ______

If yes, does the well network have sufficient well density and the proper distribution of wells to identify the impacts of that anisotropy on amendment distribution?

d) Effectiveness in Reactions with Site Contaminants/Modification of Subsurface Conditions

Are COC concentrations decreasing at a statistically significant rate?____ If so, do subsequent data indicate a statistically significant reduction? ____Are COC concentrations increasing as a result of desorption? ____

Is there evidence for unexpectedly large rebounds in concentration? _____ If so, where and by what contaminant?

Where amendment delivery was adequate, are all target contaminant concentrations decreasing as expected? _______ If not, what contaminants are not degrading as anticipated?

Are there accumulations of unwanted/unexpected byproducts of degradation observed? _______ If there are some, how long may they persist?

Are other indicators of effectiveness, such as microbial counts/composition or redox conditions, changing as anticipated? _______

Is there evidence that contaminant destruction or transformation is progressing to completion or is the process stalling at an intermediate daughter product (for example, is trichloroethylene completely degraded to ethene/ethane)? _______ Or is a different degradation pathway being used (for example, abiotic)? ______

Are related changes in subsurface conditions impeding the desired reactions (for example, is pH changing in a way that inhibits microbial activity or that supports activation of persulfate)? ______

Are there other previously known compounds or recently discovered contaminants (for example, emerging contaminants such as perfluorinated compounds) that were not targeted for destruction and now need to be addressed by the remedial activities but are not amenable to destruction by the chosen amendments? ______ Describe.

6) Alternatives for Performance Improvement and Possible Cost Savings

Can the delivery of amendments (possibly in select areas with poor injection response) be improved by:

Additional characterization of hydrogeology (for example, permeable zones) or contaminant mass/extent using high-resolution site characterization to better define target areas and pathways? Is additional characterization of the microbial community required (for example, qPCR)?

Tighter spacing of injection points or injection lines based on a re-evaluation of actual delivery extent? If so, where?

Enhancing permeability in fine-grained soils or weathered bedrock by creating new delivery pathways via sand-filled fractures?

Use of recirculation (paired pumping and injection of amended liquid)?

Targeting more specific vertical intervals?

Altering sequence/locations of injection to address displacement of contaminants (for example, injecting from the outside in)?

Use of a different delivery method (for example, use of permanent points can reduce injection if many rounds of injection are planned)?

Reduction of injection pressures (to reduce inadvertent injection outside of the target zone, excessive daylighting)?

Rehabilitation of permanent injection points to address poor injection performance?

Can the adequacy of the amount and type of amendment delivered to the target zone be improved to allow desired concentration declines and amendment persistence by:

Increasing volume of injected amendment per injection point?

Increasing the concentrations of the amendment (though care must be taken to avoid negative buoyancy issues, auto-decomposition of the amendment, or toxicity issues with bioaugmentation cultures)?

Changing the type of amendment (for example, emulsified vegetable oil rather than lactate solution for reductive dechlorination)?

Addition of different but appropriate buffers, activators, etc.?

Can the destruction of all contaminants, including byproducts of reaction or any newly discovered contaminants, be enhanced by:

Adding other amendments to improve performance or address other contaminants (for example, bioaugmentation, different activator chemical for oxidants, a buffer to control pH)?

Completely changing the amendment (for example, replacing a carbon source with a chemical reductant)?

Using a form of the amendment that has a longer life span in the subsurface (for example, permanganate rather than a modified Fenton's reagent or emulsified vegetable oil rather than lactate)?

Switching to an amendment that has a lower cost for similar performance?

Can the remedy be better implemented and managed through changes in the performance and operational monitoring, including:

Adding more monitoring points in critical areas inside and outside the TTZ?

Increasing frequency of monitoring of concentrations of contaminants, amendments, or other indicators (frequency may depend on the expected rate of change in contaminant or amendment concentrations)?

Adding other performance parameters (for example, genetic testing such as QuantArray, oxidation/reduction potential, isotopic data, byproducts of treatment) or sampling of other media (for example, soil, soil gas)?

Decreasing sampling frequency, locations, and analytes to reduce costs, particularly for projects that have been undergoing treatment for an extended time period?

More detailed monitoring of injection volumes, pressures, and depths to assess adequacy of delivery of amendments (digital recording offers much more detail)?

Taking steps to reduce daylighting of amendments and/or to develop better plans for addressing spills/discharge of amendments and potentially contaminated media at the surface, especially where there are old boreholes, pits, etc., that could be conduits?

Does the injection equipment/crew have the capability to adequately address the project?

Is the equipment/crew provided for additional injections at the site capable of delivering and documenting reagents in conformance with the design and field performance expectations?

Do the contract specifications or plans for future work need to add more specific directions/requirements to ensure the equipment/crew would be suitable to meet the performance expectations?

7) Supplemental Notes and Data. Attach any additional notes, data, calculations, etc., to this checklist.

Appendix G. Optimizing Injection Strategies and In situ Remediation Performance

Optimizing Injection Strategies and In situ Remediation Performance SurveyMonkey

Q4 Check the reasons for the incomplete determinations for t… identified in the previous questions. Check all that apply or ad… reasons.

Answered: 114 Skipped: 8

Optimizing Injection Strategies and In situ Remediation Performance SurveyMonkey

Q2 How many in situ remediation projects have you been involved with designing, implementing, and/or regulatory review?

Answered: 121 Skipped: 1

ANSWER CHOICES	RESPONSES	
0	2.48%	3
1 - 25	64.46%	78
26 - 50	14.88%	18
51 - 75	4.13%	5
76 - 100	8.26%	10
Greater than 100	5.79%	7
TOTAL		121

Optimizing Injection Strategies and In situ Remediation Performance SurveyMonkey

…egulatory authority issued the required permits or approvals. 1 is the most frequent and 3 is the least frequent

Answered: 116 Skipped: 6

[*Click here*](#) to view the entire Appendix G in Adobe PDF format.

The links below will open individual survey questions.

[Q1](#)
Identify your affiliation

[Q2](#)
How many in situ remediation projects have you been involved with designing, implementing, and/or regulatory review?

[Q3](#)
From the number of projects identified in the previous question; what percentage of projects did not provide adequate information in the first submittal to demonstrate the selected remedy would be successful?

[Q4](#)
Check the reasons for the incomplete determinations for the projects identified in the previous questions. Check all that apply or add additional reasons.

[Q5](#)
What was the root cause(s) for the inadequate information provided in those projects that did not support the selected remedy?

[Q6](#)
Which regulatory authority issued the required permits or approvals. 1 is the most frequent and 3 is the least frequent

[Q7](#)
Please include your contact information in case clarification is required

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Glossary

A

amendment (combination of reagents), or: The term amendment can refer to chemical compounds, natural or chemical additives, and/or commercially branded remediation products used for the purpose of achieving remediation goals and objectives.

B

Background demand of oxidant – is defined as reduced minerals (i.e. ferrous iron, manganous manganese), naturally occurring organic material, and/or other non-targeted, but organic contaminants that are present in the subsurface and will readily react with the added oxidant thereby consuming it.

E

emplacement – modify the subsurface permeability by pressurized application of a slurry.

I

injectate (that which has or will be emplaced including non-active ingredients/reagents such as carrier water and tracer)

injection – deliver a soluble amendment through pore space

P

Performance Indicator – A performance indicator is a measurable or calculable feature of a remedial system or process that provides direct interpretive value to (1) remedial mechanisms or processes or (2) achievement of a remedial objective. A performance indicator should be defined in terms of the technology being used, targeted media, receptor location, and expected response of the subsurface to treatment by the technology. Typically and historically, a performance indicator is the contaminant concentration; however, other performance indicators may provide information regarding the mechanisms responsible for decreases in contaminant concentration (e.g., percent of groundwater plume capture to demonstrate plume containment, mass flux to demonstrate source control, NAPL depletion rate, biodegradation rate).

Performance Metric – A metric is a unit of measure; therefore, a performance metric is the unit of measure for a performance indicator.

Performance Model – A performance model is a predictive model that describes the expected course of the remediation process. It describes graphically and/or numerically how conditions are expected to change over time, as measured using appropriate performance indicators, from the current state until the performance objective is achieved. At many sites and for many remedial systems, no single performance model, indicator, and metric is likely to be adequate for assessing remedial performance; thus, conjunctive use of multiple metrics may be needed to evaluate performance.

R

Reagent (individual active ingredient)

Remedial System Performance Objective – Performance objectives include specific measures used to determine whether or not the remedial action is successful in achieving site-related remedial goals or interim remedial milestones. Remedial performance objectives typically are site and technology specific, and based on the site-related remedial goals. They also vary depending on the type of contaminant being remediated (e.g., chlorinated volatile organics, petroleum hydrocarbons, metals, PCBs). When developing remedial system performance objectives, the practitioner should consider how the data will be used to evaluate progress, guide optimization, and demonstrate achievement of site remedial goals.

S

A **secondary water quality impact** is a change in the water chemistry caused by the added amendment which was not intended or designed for which creates a potential (and likely temporary) deterioration in water quality with respect to human and ecology health considerations or the objectives of the remedial treatment regime.

T

Target demand – The amount of amendment required to destroy the target contaminant.

W

Whip Checks act to control whipping in the event of a failure. Spring-loaded loops in the cable ends open easily to pass over the couplings, for a firm grip on the hose.

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