Naval Facilities Engineering Systems Command

USER GUIDE
FINAL

OPTIMIZING REMEDIATION TECHNOLOGIES

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14. ABSTRACT
The objective of every remedial action operation program should be to achieve cleanup standards as cost-efficiently as possible. To ensure that progress is made toward achieving cleanup standards through active remediation, technology-specific guidance for optimizing 15 selected remedial technologies is presented in this document. For each technology, this document provides a description, an example performance plot, and a summary of common operational problems and corresponding optimization recommendations.

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DISCLAIMER

ACRONYMS AND ABBREVIATIONS

AC	activated carbon
AFCEE	Air Force Center for Engineering and the Environment
AFVR	aggressive fluid-vapor recovery
AOP	advanced oxidation process
AS	air sparging
bgs	below ground surface
BTEX	benzene, toluene, ethylbenzene and total xylenes
CMC	carbonxylmethyl cellulose
CRD	Catalytic reductive dechlorination
CSM	conceptual site model
CVOC	chlorinated volatile organic compound
DCE	dichloroethene
DNAPL	dense nonaqueous phase liquid
DO	dissolved oxygen
DoD	Department of Defense
DPT	direct push technology
DPT-JI	direct-push technology jet injection
DRMO	Defense Reutilization and Marketing Office
EISB	enhanced in-situ bioremediation
EK	electrokinetics
ERH	electrical resistance heating
EVO	emulsified vegetable oil
FOC	fraction of organic carbon
FRTR	Federal Remediation Technologies Roundtable
GAC	granular activated carbon
Hg	mercury
HRC	hydrogen release compound
ISBGT	in-situ biogeochemical transformation
ISCO	in-situ chemical oxidation
ISCR	in-situ chemical reduction
LIF	laser-induced fluorescence
LNAPL	light non-aqueous phase liquid
MBT	microbiological tool
MCAS	Marine Corps Air Station

MNA	monitored natural attenuation
MPE	multi-phase extraction
MTBE	methyl tertiary-butyl ether
NAPL	nonaqueous phase liquid
NAS	Naval Air Station
NAWS	Naval Air Weapons Station
nm	nanometer
NSZD	natural source zone depletion
ORC	oxygen release compound
OU	Operable Unit
P&T	pump and treat
PAH	polycyclic aromatic hydrocarbon
PCB	polychlorinated biphenyl
Pd	palladium
PFAS	per- and polyfluoroalkyl substances
PFOA	perfluorooctanoic acid
PFOS	perfluorooctane sulfonate
POTW	publicly owned treatment works
PRB	permeable reactive barrier
psi	pounds per square inch
RA-O	remedial action operation
ROD	Record of Decision
RPM	Remedial Project Manager
SEE	steam enhanced extraction
SVE	soil vapor extraction
SVOC	semivolatile organic compound
TCE	trichloroethene
TCH	thermal conductive heating
TCRA	time critical removal action
TPH	total petroleum hydrocarbons
UV	ultraviolet
VC	vinyl chloride
VI	vapor intrusion
VMP	vapor monitoring point
VOC	volatile organic compound
WWTP	wastewater treatment plant

ZVI	zero valent iron
ZVZ	zero valent zinc

1.0 INTRODUCTION

The objective of every remedial action operation (RA-O) program should be to achieve cleanup standards as cost-efficiently as possible. To ensure that progress is made toward achieving cleanup standards through active remediation, technology-specific guidance for optimizing 15 selected remedial technologies is presented in this document. This document includes an overview of the following information for each selected remedial system:

- A brief system description.
- An example performance plot.
- A table outlining common operational problems and typical optimization recommendations.

References are provided where additional details can be found regarding design, implementation, and optimization of the remedial technologies. Examples included in this document are taken from case histories of remedial actions that were evaluated using the RA-O optimization process.

Conventional remedial systems that have wide application such as pump and treat (P&T), soil vapor extraction (SVE), and air sparging (AS) are presented first. Discussions of these remedial systems are followed by those of more innovative technologies and less commonly applied systems. This document also includes an overview on utilizing monitored natural attenuation (MNA) as an alternative to or following active remediation systems. Finally, the document addresses various above ground components commonly used in treating vapor phase and liquid phase waste streams.

Before a remediation system is optimized, it should be evaluated against the criteria described in Sections 2.0 through 5.0 of the *NAVFAC Guidance for Optimizing Remedial Action Operation* (NAVFAC, 2012) to first determine if the underlying technology is capable of achieving the site cleanup goals. The results of the evaluation must show that the operation of the existing remediation system is consistent with the overall remedial strategy and cleanup objectives for the site. If the results of the evaluation do not verify the effectiveness of the existing technology, the Remedial Project Manager (RPM) should consider changing to a different remedial technology and proceed to make this case to the regulatory agency. Optimization of a system to improve its efficiency is justifiable only when it can be verified that the current technology is capable of achieving the cleanup objectives in a reasonable amount of time. For instance, no degree of optimization will improve the operational efficiency of an SVE system at a fuel release site where the remaining contaminants are semivolatile organic compounds (SVOCs), which are not removed by SVE. In such a case, it would be more appropriate to adopt a different technology that is known to be effective against these contaminants than to attempt to optimize the SVE system.

Technology-specific guidance for optimization is presented in this document to ensure that remediation systems that are verified to be operating effectively are also operating efficiently. For each of the selected technologies, a brief description of the system and a discussion of performance evaluation are presented. These are followed by discussions of common operational problems and optimization strategies applicable to each technology, including:

- Pump and Treat (P&T)

- Soil Vapor Extraction (SVE)
- Air Sparging (AS)
- Bioventing
- Multi-Phase Extraction (MPE)
- Free Product Recovery
- Natural Source Zone Depletion (NSZD)
- Phytoremediation
- Permeable Reactive Barriers (PRBs)
- In-situ Adsorbents
- Enhanced In-situ Bioremediation (EISB) – Aerobic, Anaerobic, and Co-metabolic
- In-situ Chemical Oxidation (ISCO)
- In-situ Chemical Reduction (ISCR)
- In-situ Thermal Treatment
- Monitored Natural Attenuation (MNA).

2.0 PUMP AND TREAT

2.1 System Description

P&T technology involves the retrieval of groundwater from a contaminated aquifer using one or more extraction wells, trenches, or galleries, and treating the water in an above ground treatment system prior to discharge (FRTR, 2020). Groundwater P&T systems are used to either: 1) hydraulically contain the migration of a plume of dissolved contaminants, 2) remove dissolved contaminants from the saturated zone, or 3) implement a combination of containment and removal. P&T systems can be employed to treat a wide variety of contaminants present in the dissolved phase, including volatile organic compounds (VOCs), SVOCs, metals, and also per- and polyfluoroalkyl substances (PFAS). The number of P&T systems operating has been declining over recent years, and often other more efficient and sustainable remedial technologies are available, particularly to accomplish mass reduction within a contaminant plume.

P&T systems may still be identified as an effective remedy to achieve hydraulic containment in situations where site conditions preclude aquifer restoration, such as aquifers contaminated by dense nonaqueous phase liquid (DNAPL). Containment may also be used as an interim approach to protect receptors while a mass removal technology is active in a part of the plume. These systems incorporate wells equipped with pumps to extract groundwater and create a hydraulic capture zone that prevents horizontal and vertical migration of a contaminant plume. The extraction wells establish a capture zone by depressing water levels to form areas of low hydraulic head toward which the contaminated groundwater flows.

Pump and treat systems typically include the following components:

- An extraction network, including wells and/or trenches.
- A collection system, including groundwater pumps and conveyance piping.
- An extracted groundwater treatment system and disposal option.
- A monitoring system and program.

Figure 2-1 is a schematic diagram of a P&T system using extraction and reinjection wells to hydraulically contain a plume. A pre-treatment unit, air stripper, and liquid-phase granulated activated carbon are used to treat extracted groundwater in this system prior to discharge. Treatment options for extracted water are presented separately in Section 18.

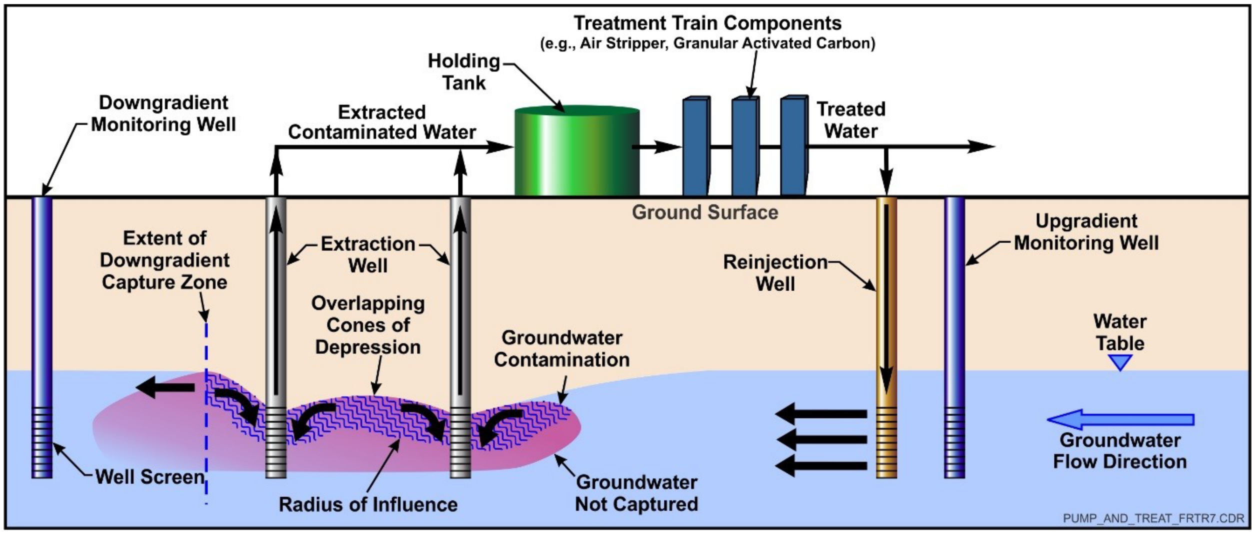


Figure 2-1. Typical Pump and Treat System (FRTR, 2020)

2.2 Performance Plots

The effectiveness of a P&T system for hydraulic containment is assessed by periodically measuring and evaluating water levels (hydraulic head) and groundwater quality in the monitoring well network to verify that the contaminant plume is not migrating. Delineating the horizontal capture zone alone is adequate for hydraulic containment systems utilizing extraction wells that fully penetrate an aquifer. However, delineating the vertical capture zone using data collected from nested monitoring wells is also necessary if the extraction wells are only partially penetrating.

Evaluating the effectiveness of hydraulic containment systems involves comparing water levels within and beyond a plume to verify that inward gradients have been established. Inward gradients indicate that groundwater flow is toward the extraction wells and ensure that dissolved contaminants are captured by the extraction well network. The performance evaluation also involves examining contaminant concentrations and trends in monitoring wells, especially in those wells located near the edge of the plume, to verify that no contaminant migration is occurring. The water level and water quality data are most easily evaluated using maps and cross-sections to plot the potentiometric surface and contaminant extent. The presence of inward gradients can be interpreted from the potentiometric contour maps and cross-sections. Similarly, contaminant extent can be plotted to determine if the size and position of a plume remain stable. Overlaying the potentiometric contours onto the contaminant distribution map indicates if the entire plume is located within the hydraulic capture zone. Figure 2-2 is a generalized plot showing a contaminant plume that is under the hydraulic control of a P&T system. The diagram also shows 12 monitoring wells for measuring water levels and collecting groundwater samples for chemical analysis to evaluate the effectiveness of the P&T system. The figure indicates that the entire plume is located within an area where potentiometric surface contour lines depict the presence of inward gradients.

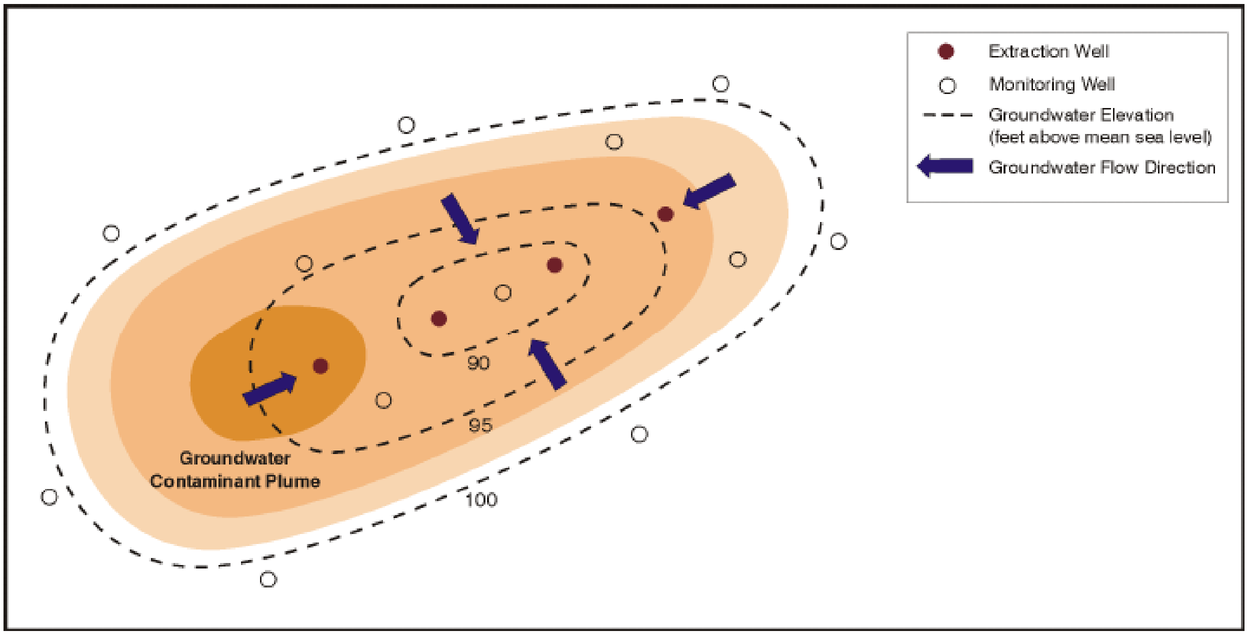


Figure 2-2. Performance Plot of a Typical Pump and Treat System for Hydraulic Control

Historical data have demonstrated that the use of pump and treat systems is generally considered to be inefficient for purposes of mass removal, and more recent Records of Decisions (RODs) have increasingly selected in-situ treatments over P&T to address contaminant mass in groundwater. For those existing RODs with remedial goals for mass removal using P&T, two major limitations are often observed, including phenomena known as tailing and rebound.

The tailing effect is exhibited as a gradual decline in the rate at which contaminant concentrations in the influent are reduced. A plot of concentrations versus time for these systems will have an area of high initial contaminant concentrations, followed by a period of rapidly declining concentrations, and finally a period in which influent contaminant concentrations reach asymptotic levels. Figure 2-3 shows a performance plot for a P&T system that has achieved an asymptotic level in the concentration of some extraction wells. Similar plots should be prepared for individual monitoring wells by graphing contaminant concentrations in groundwater samples versus time. The concentrations in monitoring well plots will also eventually reach asymptotic levels as pumping continues.

When pumping is terminated for at least several months, the contaminant concentrations in the groundwater will typically rebound to levels that exceed those measured during system operation, but which are below initial concentrations. The rebound in concentrations will be evident in monitoring well samples and in the influent of a system that is restarted. Figure 2-4 illustrates several periods of rebound in the influent concentration of a P&T system that is alternately turned on and off in an operating procedure known as pulsing.

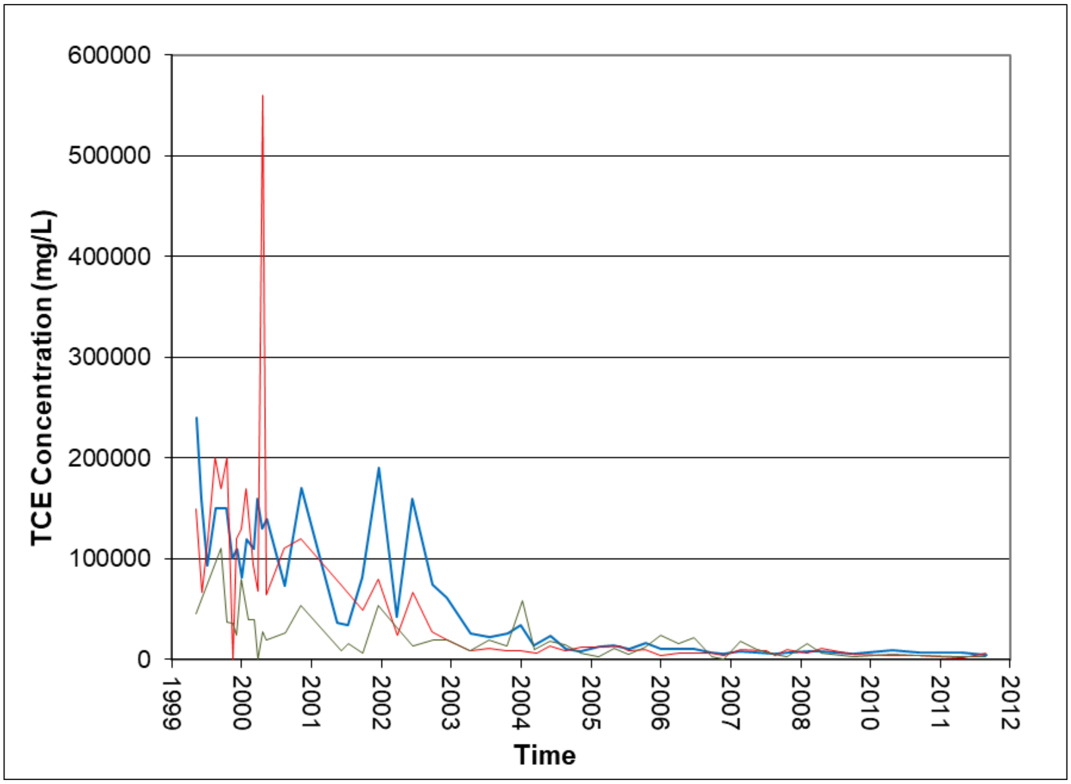


Figure 2-3. Performance Plot of Select Groundwater Pump and Treat Extraction Wells, Former Naval Air Warfare Center Warminster, Pennsylvania

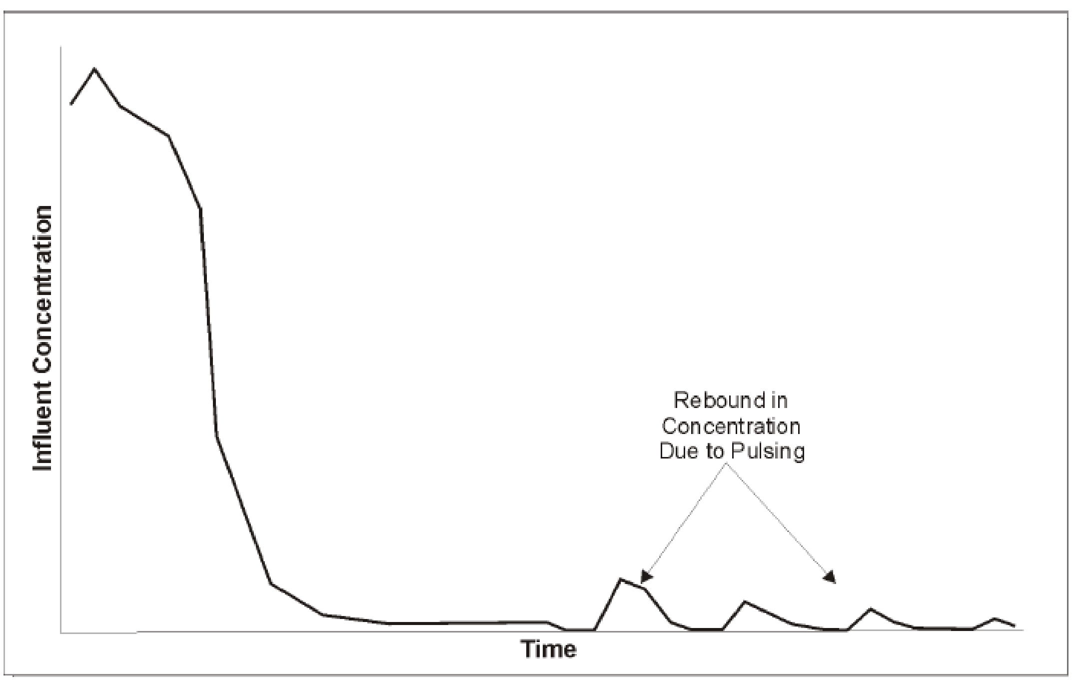


Figure 2-4. Typical Performance Plot Showing Rebound in Influent Concentration as a Result of Pulsing a Pump and Treat System

2.3 Common Operational Problems

An unrealistic expectation that a P&T system alone can attain cleanup goals based on drinking water standards is a fundamental problem common to many sites. Practical application of the technology has shown that the feasibility of achieving cleanup to drinking water standards using P&T systems is difficult. P&T systems are most likely to achieve this goal at sites involving mobile contaminants dissolved in groundwater in a permeable, homogeneous aquifer from which the source area has been completely removed. However, even under these ideal conditions several factors, including the presence of residual contaminants, slow contaminant desorption, and low hydraulic conductivity, can impose serious limitations on P&T performance. These factors contribute to the tailing and rebound effects described above. Both tailing and rebound increase the volume of water that must be extracted to achieve cleanup goals and, therefore, prolong the time necessary to complete remediation.

The contaminant source, including any nonaqueous phase liquid (NAPL) present at residual saturation, should be removed to the extent possible before a P&T system can potentially restore an aquifer. Otherwise, contaminants in the source area will continue to dissolve into groundwater and maintain concentrations above cleanup goals. Similarly, as pumping progresses and reduces the concentration of contaminants dissolved in groundwater, any contaminants sorbed to the aquifer matrix will partition into groundwater at rates that depend on the contaminant concentrations, their sorption properties, and the velocity of groundwater flow. When pumping first commences, increased groundwater flow rates cause a decrease in contaminant concentrations that ultimately tails off until the rate of desorption is again in equilibrium with the increased groundwater flow velocity. This tailing phenomenon is responsible for the asymptotic contaminant concentration levels typically seen in the performance plots of many P&T systems. Subsequently, if pumping is terminated, groundwater flow velocity decreases, contact time between the sorbed contaminants and groundwater increases, and dissolved contaminant concentrations rebound as higher equilibrium conditions are re-established.

Asymptotic mass removal becomes an issue when further system operation does not reduce contaminant levels below the final clean-up goals in a reasonable timeframe, resulting in high unit mass removal costs. Several fate and transport processes occurring within an aquifer or vadose zone contribute to asymptotic mass removal behavior, including geologic and flow limitations and contaminant property limitations (NAVFAC, 2001). Research, including laboratory testing performed by Colorado State University and Colorado School of Mines, indicates that a significant portion of contaminant mass is driven into stagnant silt layers and then subsequent back diffusion from these stagnant zones sustains contaminant discharge for prolonged periods of time (Air Force Center for Engineering and the Environment [AFCEE], 2007).

Other operational problems common to P&T systems are those associated with the extraction well network. Decreased well yield is a particularly common problem that can result from screen incrustation and biological fouling. Corrosion is another cause of lowered well performance that can lead to screen failure, sand pumping, and pump damage. Regular measurement of well depth and specific capacity can provide warning of impending problems and indicate the need for well maintenance. Table 2-1 lists other problems common to P&T systems for contaminant removal.

In some cases, specific capacity can decrease to levels at which the desired flow rate can't be achieved. The cross-section in Figure 2-5 compares the following: 1) an expected drawdown curve (Curve No. 1) and 2) a well where the screen and filter pack have become clogged resulting in a decreased drawdown through the formation and substantial increase in drawdown through the well screen (Curve No. 2).

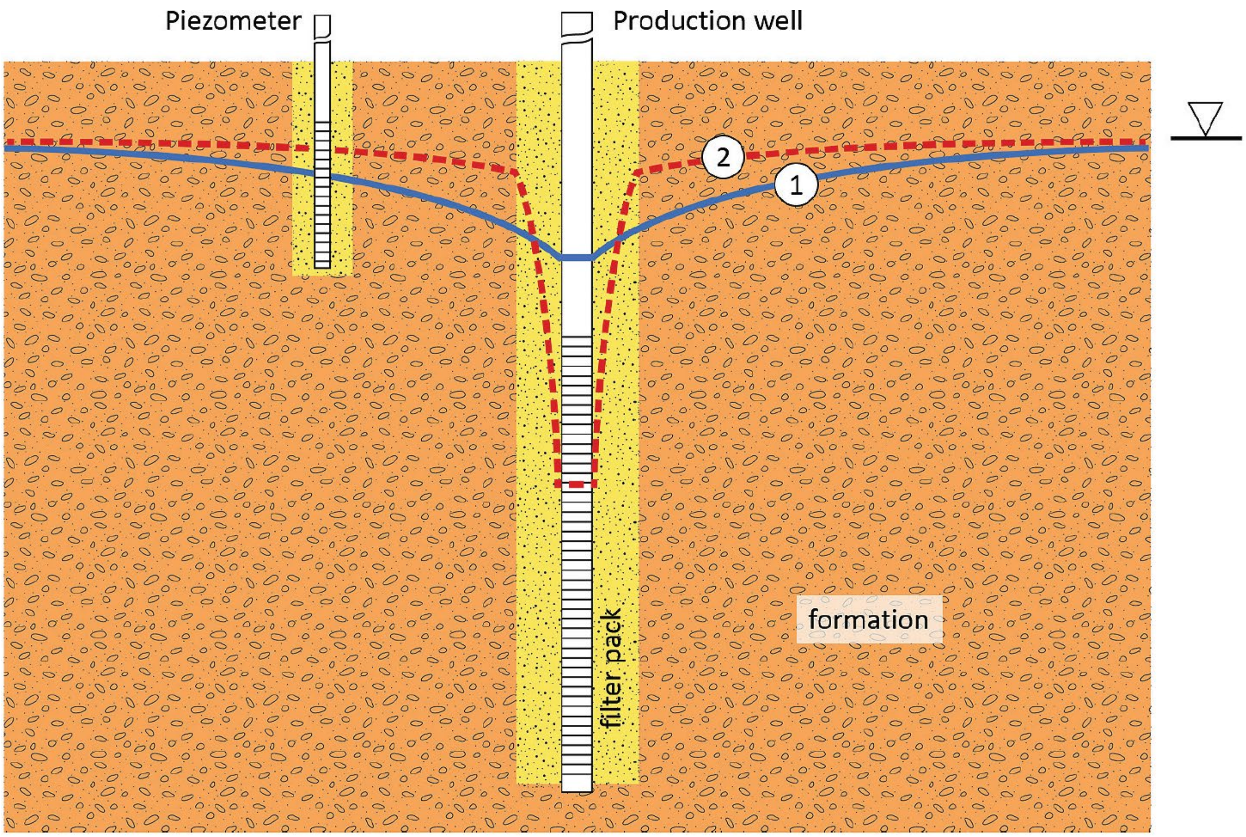


Figure 2-5. Change in Well Efficiency Due to Fouling in the Well Screen and Filter Pack

Table 2-1 lists these and other problems common to P&T systems.

2.4 Common Optimization Strategies

Asymptotic levels of mass removal are often reached by P&T systems; therefore, the most significant optimization strategy is to evaluate alternative remedial technologies for source treatment that may be more cost-effective, including MNA. If that is not an appropriate option, another strategy is to alternate periods of pumping with periods of no pumping in a procedure known as pulsing. During each non-pumping period, contaminants sorbed to the aquifer matrix or residing in low permeability zones are allowed to reach chemical equilibrium in the groundwater resulting in the removal of the highest contaminant concentration for the minimum volume of water extracted. During pulsing, hydraulic containment must be maintained to prevent contaminant plume migration. In some cases, the plume may not migrate beyond the radius of the capture zone before pumping is resumed and inward gradients are re-established. In other cases, however, the plume may need to be contained by continuously pumping wells near the boundary while wells in the more highly contaminated portions of the plume are pulsed.

Where containment is the goal of P&T, optimization efforts are focused on ensuring that the minimum quantity of groundwater is extracted to maintain plume containment. At sites with large dilute plumes requiring containment, the evaluation of alternative risk management strategies and/or the use of MNA may be appropriate to optimize groundwater extraction rates. For example, the development of alternate concentration limits based on fate and transport modeling, natural attenuation occurring within the aquifer, and mixing within a downgradient surface water discharge location may result in needing to contain only a portion of the larger plume while still being protective against potential risks to receptors. Details regarding the use of alternative risk management strategies is discussed in Section 6.3 of the *NAVFAC Guidance for Optimizing Remedial Action Operation* (NAVFAC, 2012).

Some systems are operated at the maximum achievable extraction rates whether warranted or not. For other systems, excessive amounts of water may be extracted if the hydraulic containment design analysis was performed at a time when groundwater elevations were below normal or when the source concentrations were higher and the aerial extent of the plume was larger. One remedy to these situations is to ensure that the conceptual site model (CSM) is consistently updated with each new round of monitoring data and to readjust the pumping rate and monitor the hydraulic response. The rate can be adjusted over a series of incremental steps until monitoring indicates that the lowest rate capable of maintaining capture has been attained. Another remedy that may be appropriate to highly characterized sites is to perform optimization modeling using analytical or numerical techniques. Available models range from simple graphical methods to complex models that have been combined with linear and nonlinear programming methods. Additional information regarding tools available for such modeling can be found in Section 9.11 of the *NAVFAC Guidance for Optimizing Remedial Action Operation* (NAVFAC, 2012). At some sites, high long-term operating costs may justify installing low permeability barriers that limit the flow of clean water into contaminated portions of the aquifer and allow pumping rates to be decreased significantly. Table 2-1 lists factors that should be considered to optimize the performance of P&T systems.

Other optimization strategies are related to improving the operation of the extraction wells (NAVFAC, 2017a). Decreasing well yield is a particularly common problem that can result from screen incrustation and biological fouling. Corrosion is another cause of lowered well performance that can lead to screen failure, sand pumping, and pump damage. Regular measurement of well depth and specific capacity can provide warning of impending problems and indicate the need for well maintenance.

Example: *At Naval Air Station (NAS) Brunswick, "uptime" for wells in the Eastern Plume P&T system was limited by high turbidity and "sand pumping." The operational history of the system indicated that these were recurring problems in wells whose design and construction required that the pumps be located in or near the screened portion of the wells. Therefore, it was recommended that the pumps be positioned above the well screen in all suitably constructed existing wells and in any new wells added to the system.*

Table 2-1. Common Operational Problems and Optimization Strategies for Pump and Treat Systems

Operational Problem	Potential Causes	Potential Negative Impacts on Performance	Optimization Strategy
The contaminant concentrations have not declined in the system influent and in the monitoring wells.	• Source areas or hot spots have not been adequately treated. • The pumping rate is too low to allow an adequate number of pore volumes of groundwater to be pumped through the contaminant plume.	• The inability to remove contaminants due to ineffective flushing or lack of source control precludes aquifer cleanup.	• Evaluate alternate technologies for possible implementation. • Increase the pumping rates of existing wells and/or install additional wells to increase the number of pore volumes pumped through the contaminant plume. • Install source control wells or evaluate other source treatment options.
The contaminant concentrations in the system influent and in the monitoring wells have reached asymptotic levels and/or rebound to higher levels when pumping is terminated.	• The removal of contaminants sorbed to the aquifer matrix is limited by site-specific desorption rates. • The removal of contaminants within low permeability zones is diffusion limited. • The extraction wells are improperly located or continue to operate in areas where contamination has been reduced. • The extraction wells are inappropriately screened through zones of lesser contamination. • The contaminants remain at stagnation points that are not flushed by groundwater pumping.	• The slower rate of contaminant removal will extend cleanup time.	• Evaluate alternate technologies for possible implementation. • "Pulse" the extraction wells or reduce the pumping rates to correspond to contaminant desorption and/or diffusion rates. • Identify unproductive extraction wells through sampling and decrease the pumping rates while increasing rates at more productive wells. • Replace the improperly screened wells with wells isolated to the contaminated intervals within the aquifer. • Rebalance the pumping rates between wells to eliminate stagnation points or install additional wells to enhance flushing through stagnation points.
The system is not effectively removing contaminants, but the contaminant concentrations are decreasing or have reached asymptotic levels and the plume is stable or receding.	• The contaminants may be undergoing natural attenuation.	• Continued active remediation may not be cost effective.	• Evaluate the feasibility of MNA for site remediation. Shut down the pump and treat system if MNA is feasible.
The extraction rate declines over time.	• Mineral incrustation of the well screens is occurring. • Biological fouling of the well screens is occurring.	• Pumping below the design rate can result in a capture zone that shrinks in size and fails to maintain hydraulic containment.	• Perform well rehabilitation using appropriate acids and/or biocides. • Redevelop the affected wells. If fouling reoccurs, establish a preventative maintenance program to redevelop wells on a regularly scheduled basis.

Table 2-1 (continued). Common Operational Problems and Optimization Strategies for Pump and Treat Systems

Operational Problem	Potential Causes	Potential Negative Impacts on Performance	Optimization Strategy
The design extraction rates have never been achieved in individual wells.	• The pumps are not properly sized. • The extraction wells were improperly designed, installed, or developed. • The aquifer yield is less than predicted.	• The inability to achieve the design rate may result in a failure to establish a capture zone of sufficient size to contain the contaminants.	• Install properly sized pumps. • Redevelop the poorly developed wells. • Replace the wells that are improperly designed or constructed. Use high-flow screen materials whenever possible. • Review and potentially revise the aquifer testing results. Install additional wells, as necessary to achieve adequate hydraulic containment.
The wells are pumping sand or experiencing siltation.	• The pumps are improperly placed within the well screens. • The wells are poorly developed. • The wells were installed with inadequate sand packs or screen slot size.	• "Sand pumping" can lead to excessive well or treatment system downtime and result in the loss or diminished size of the capture zone.	• Raise the pumps above the well screens and redevelop the affected wells. • Redevelop the poorly developed wells. • Replace the improperly installed wells, ensuring proper filter pack design.
The contaminant plume is migrating.	• The pumping rate is not sufficient to establish a capture zone. • The system is experiencing prolonged downtime. • The number of wells is not adequate or they are improperly located.	• Failure to maintain containment will allow the plume to expand in size and potentially reach receptors.	• Increase the well pumping rates. • Increase the system uptime through a preventive maintenance program. • Install additional wells.
Excessive volumes of water are being extracted.	• The system is arbitrarily being pumped at the maximum rate or the margin of safety in the pumping rate is overly conservative. • The design rate was based on an analysis of abnormal conditions or when the extent of the contaminant plume was larger. • The high permeability of the aquifer requires a high pumping rate to maintain the capture zone.	• Pumping at rates greater than required to contain the plume results in unnecessary costs.	• Incrementally adjust pumping to lower rates and monitor the hydraulic response until results indicate that the minimum pumping rate necessary to maintain the capture zone has been attained. • Adjust water level set points based on the target water table drawdown required to contain the plume. • Keep CSM up to date. • Perform analytical or numerical groundwater modeling to calculate optimum pumping rates and water level set points. • Evaluate whether installing low permeability barriers will be cost effective in lowering the pumping rate in high yielding aquifers.

3.0 SOIL VAPOR EXTRACTION

3.1 System Description

SVE involves the application of a vacuum in the vadose zone to induce the controlled flow of air and removal of volatile and some semivolatile contaminants from the subsurface (FRTR, 2020). SVE is applied to vadose zone soils, generally within source areas of contamination. This technique is most effective in soils with relatively homogenous soil lithology and high permeability to air. It is not effective where the water table is less than 3 feet below ground surface (bgs) and requires special controls such as groundwater pumping or horizontal wells at sites where the water table is less than 10 feet bgs. SVE wells are installed and screened above the water table and should intersect the subsurface zone(s) of contamination as much as possible. The application of a vacuum to these wells induces air to flow from the atmosphere, through the contaminated vadose zone, and to the well screen. This flow of air causes contaminants with low vapor pressures to be volatilized from subsurface soils into the vapor phase and transported to the surface where the VOCs can be treated and/or discharged.

The primary components of a typical SVE system (Figure 3-1) include extraction wells, transfer piping, a water-vapor separator, a vacuum pump/blower, and a vapor treatment system. The figure also illustrates an air inlet well, which is sometimes included in the system design to enhance airflow in the subsurface. Most of the differences between individual SVE systems are associated with the type and size of the vacuum generating system and the vapor treatment system. The types of vacuum pumps/blowers typically used include regenerative, positive displacement, and liquid ring. SVE wells can be readily installed as vertical wells, angled wells, or horizontal wells depending on site-specific conditions. Treatment methods for extracted vapors include direct discharge (no treatment), carbon adsorption, and oxidation. Treatment options for extracted vapor are presented separately in Section 18.

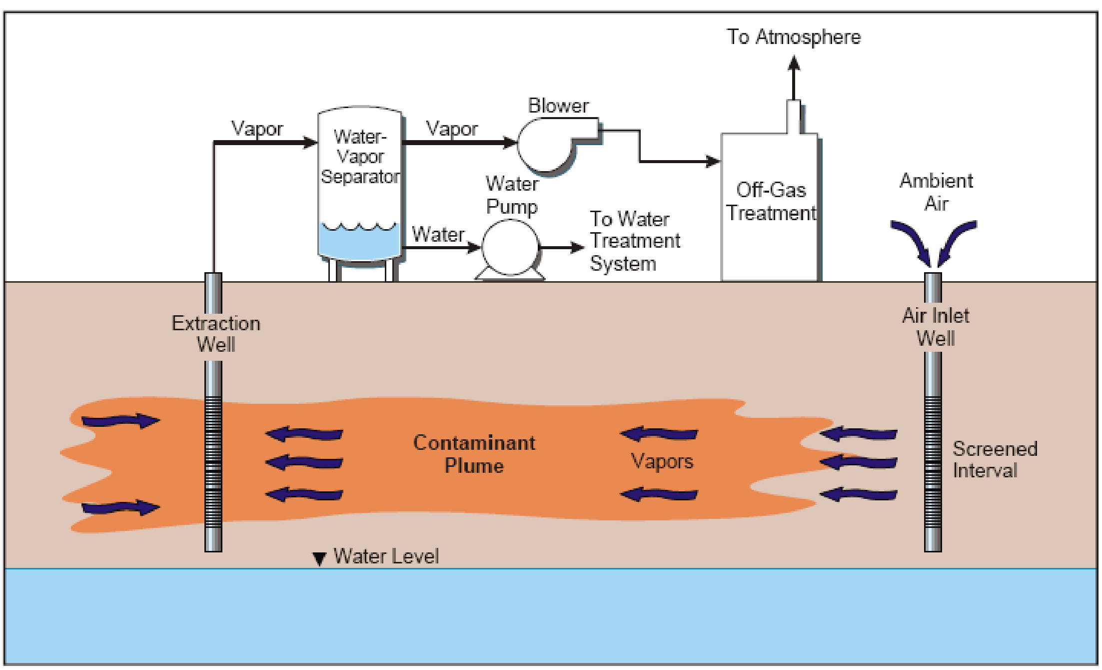


Figure 3-1. Typical Soil Vapor Extraction System

3.2 Performance Plots

Common operation and monitoring data collected to evaluate the effectiveness and efficiency of SVE systems includes the following:

- Concentration of contaminants extracted prior to treatment.
- Concentration of contaminants from each well.
- Total system vacuum and individual well vacuums.
- Condensate production rate.
- Vapor flow rate at vacuum pump inlet and from individual wells.
- Vacuum influence and contaminant concentrations at soil gas vapor monitoring points (VMPs).
- Contaminant concentrations from groundwater samples.

Vacuum isopleth maps can be prepared to determine if the vacuum distribution is consistent with design expectations and also to demonstrate the capture of vapors and the prevention of contaminant migration to receptors. The performance of SVE systems can be illustrated by plotting both contaminant vapor concentration and cumulative mass removal versus time. A typical contaminant concentration response curve for an SVE system is characterized by an area of initially high soil vapor concentrations in the extracted vapor, followed by a period of rapidly declining vapor concentrations, and finally a period in which influent vapor concentrations reach asymptotic low levels. A plot of cumulative contaminant mass removed by a SVE system is a mirror image of the contaminant concentration response curve. A plot of cumulative mass recovered versus time is shown in Figure 3-2.

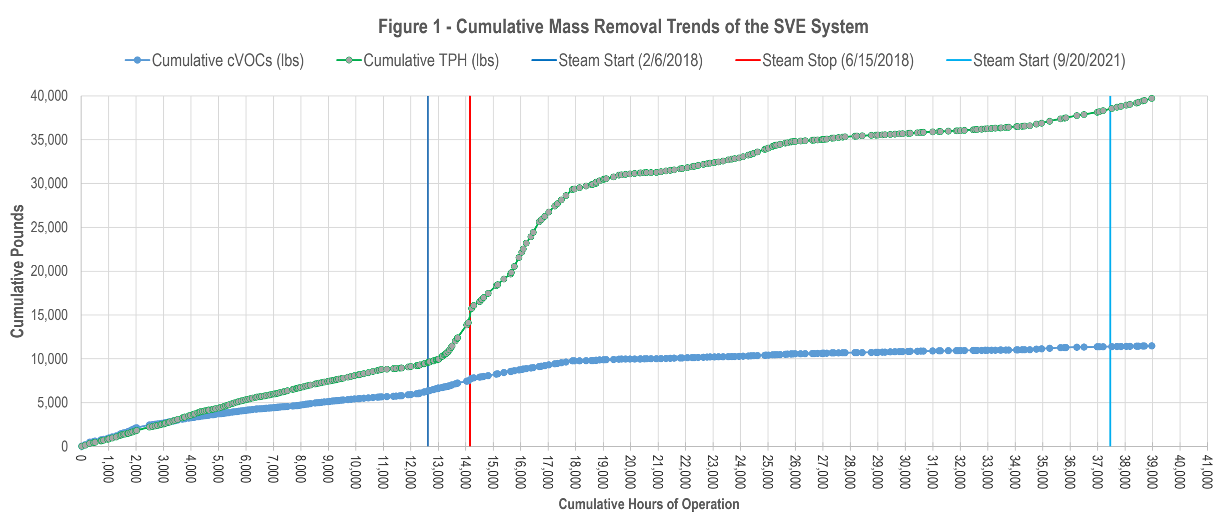


Figure 3-2. Soil Vapor Extraction System Performance at NAS North Island

Example: *A SVE system was installed as part of a time critical removal action (TCRA) to address vapor intrusion (VI) of chlorinated VOCs (CVOCs) at Operable Unit (OU) 20, NAS North Island. The system was designed with dual-screened horizontal SVE wells and an innovative cryogenic compression condensation unit for off-gas treatment and solvent recovery. The system effectiveness was evaluated through periodic monitoring of extracted soil vapor concentrations and tracked as cumulative mass removed over time. System optimization occurred when subsurface heating was applied from an existing steam line. Monitoring of extracted soil gas indicated that there was a significant increase in the rate of trichloroethene (TCE) volatilization and biodegradation with heating. These considerations were incorporated into the design and installation of the SVE system expansion for further treatment at OU 20. As part of the system design, building-specific VI attenuation factors were developed and used to establish site-specific cleanup goals related to the VI pathway.*

3.3 Common Operational Problems

SVE performance problems are commonly related to a system's inability to extract air from all areas of the remediation target zone or from excessive recovery of liquids. Generally, these problems are due to an under-designed system, short-circuiting, unanticipated site conditions, shallow water tables, or excessive vacuum application, respectively. Conversely, an SVE system that is operating effectively will eventually reach a point at which the mass transfer of sorbed contaminants typically becomes desorption and/or diffusion limited. Table 3-1 lists these and other problems common to SVE systems.

3.4 Common Optimization Strategies

Optimizing the operation of SVE systems requires reliable data collection on a routine basis to track both total extraction rate and the extraction rate of each individual well. Section 3.2 lists the common operating and monitoring data associated with SVE implementation. When the amount of mass recovered, or the constituent concentrations in the extracted vapor and in groundwater samples reach asymptotic conditions, pulsing the system should be considered in an effort to restore a higher mass removal rate. More aggressive measures such as installing additional extraction wells may also be evaluated. If asymptotic conditions persist after operational or system changes have been implemented continued operation of the SVE system will generally not result in the significant removal of additional mass. In this case, if further remediation is necessary, implementing another technology or MNA should be considered. Table 3-1 provides other guidance on optimizing SVE system performance. Guidance on optimizing above ground treatment of extracted vapors is provided in Section 18.

Table 3-1. Common Soil Vapor Extraction System Operational Problems and Optimization Strategies

Operational Problem	Potential Causes	Potential Negative Impacts on Performance	Optimization Strategy
The design extraction rates and/or radius of influence have never been achieved in individual wells.	• The air permeability of the soil is lower than estimated. • Short-circuiting is occurring due to the presence of preferential flow paths. • The extraction wells have been incorrectly designed or installed.	• The contaminants located outside the effective radius of the vacuum are not removed and prevent reaching cleanup goals. • The number of pore volumes of soil gas exchanged in the contaminated area is limited and results in low mass removal that increases cleanup time.	• Perform a subsurface investigation to further characterize the soil permeability and the preferential flow paths. • Utilize well instrumentation and characterization technologies to profile vertical differences in the air permeability and contaminant mass and focus well screen placement to the appropriate depth intervals (USEPA, 2018). • Install additional wells in the contaminated areas located outside the system's treatment zone. • Replace incorrectly designed or installed wells. • Evaluate the need for a surface cover to reduce short circuiting through ground surface.
The contaminant concentrations have been reduced in some but not all wells.	• Treatment may be complete in some areas of the site while a continued source of contaminants remains in other areas. • The airflow to some areas of the site is inadequate. • High soil moisture content due to surface irrigation may impact contaminant removal in some areas. •Continued source of contaminants in the area.	• Continued operation of nonproductive wells will not be cost effective. • The low airflow rates will limit mass removal and increase cleanup time.	• Shut off the low producing wells or reduce their pumping rates while increasing rates at the more productive wells. • Install additional extraction wells in the areas where airflow is not adequate. • Limit irrigation near low producing wells. • Excavate hot spot soils.
The contaminant concentrations in extracted vapor have reached asymptotic levels.	• The removal of contaminants sorbed to the soil is limited by site-specific desorption rates. • The removal of contaminants within low permeability zones is diffusion limited. • The extraction wells are not properly located or screened to treat all contaminated areas. • An uncontrolled source area continues to release contaminants.	• The slower rate of contaminant removal due to desorption/diffusion limitations will extend cleanup time. • The presence of a continuing source of contaminants will prevent cleanup.	• "Pulse" the wells or reduce airflow rates to correspond to contaminant desorption and/or diffusion rates. • Install additional wells in the contaminated areas located outside the system's treatment zone. • Install wells with screens isolated to the most productive soil layers or pack off unproductive intervals in existing wells.

Table 3-1 (continued). Common Soil Vapor Extraction System Operational Problems and Optimization Strategies

Operational Problem	Potential Causes	Potential Negative Impacts on Performance	Optimization Strategy
			• Implement source control including excavation if feasible. • Evaluate alternate technologies such as thermally-enhanced SVE or bioventing for petroleum-related contamination.
Low concentrations of contaminants are extracted during operation, but high concentrations reappear when the system is shut off.	• The removal of contaminants sorbed to the soil is limited by site-specific desorption rates. • The removal of contaminants within low permeability zones (tight soil layers) is diffusion limited. • The airflow rate is higher than necessary due to desorption and diffusion limits. • The airflow is short-circuiting due to preferential flow.	• The slower rate of contaminant removal due to desorption/diffusion limitations or preferential flow paths will extend the cleanup time.	• "Pulse" the wells or reduce the airflow rates to correspond to contaminant desorption and/or diffusion rates. • Temporarily shut off the system and perform equilibrium testing at vapor monitoring points to identify the more highly contaminated areas where SVE should be focused. • Identify and excavate any desorption/diffusion-limited hot spots, if feasible. • Evaluate alternate technologies such as thermally enhanced SVE or bioventing for petroleum-related contamination.
The contaminant concentrations in vapor monitoring points and in the extracted vapor remain high despite high mass removal rates	• An uncontrolled source area or free product may be present.	• The presence of a continuing source of contaminants will preclude cleanup.	• Perform further subsurface investigation to identify additional source areas and potential free product. • Identify and control any source areas including excavation if feasible.
The system extracts high volumes of water.	• The well screens are installed too close to the water table causing upwelling to occur. • Nearby surface irrigation may cause high soil moisture content and increased extraction of water.	• Water table upwelling may occlude well screens causing lower mass removal that extends cleanup time. • The extraction of high volumes of water may result in excessive system downtime.	• Replace the existing wells with shallower vertical wells or with horizontal wells. • Consider temporarily shutting down the system during periods of seasonal high water table. • Evaluate the use of an alternate technology that is not influenced by a high water table. • In tidally influenced areas, pulse the system to correspond active operation with low tides. • Limit irrigation near extraction wells.

4.0 AIR SPARGING

4.1 System Description

AS is a technology used to strip volatile compounds dissolved in groundwater and sorbed to soil, and to elevate dissolved oxygen (DO) levels throughout the contaminated zone and stimulate aerobic biodegradation of the contaminants in the aquifer (FRTR, 2020). Like SVE, AS is most effective in relatively homogeneous lithology with high permeability. It is also most effective with VOCs that exhibit a high Henry's law constant and will transfer easily to the vapor phase. The technology involves injecting air into the contaminated portion of the saturated zone. The air is typically injected through vertical wells completed below the water table. In some cases, however, horizontal wells may be used to remediate larger areas. The injected air results in the transfer of dissolved and sorbed VOCs to the vapor phase. Although the vapor can be vented naturally to the surface, it is usually extracted through a SVE system installed to control vapor migration. The application of air sparging in conjunction with SVE is known as AS/SVE.

Biosparging is a variation of air sparging in which air is injected at a lower rate than in AS. The sparging air flow rate required to provide sufficient air flow to enhance biological activity is site specific but is typically less than 3 standard cubic feet per minute (USEPA, 2017). The remediation objective in biosparging is not to volatilize the contaminants but rather to enhance their biodegradation by introducing oxygen. Biosparging is typically applied to petroleum products, dichloroethane (DCE), vinyl chloride (VC), and other contaminants that are biodegraded under aerobic conditions. Unlike air sparging, vapor extraction is not required because biosparging enhances biodegradation of contaminants in-situ. Biosparging is also not limited to remediating VOCs like air sparging, but can be effective in remediating SVOCs.

The primary components of a typical AS system include air injection wells, manifold piping, and a blower or air compressor. Figure 4-1 is an illustration of an AS system.

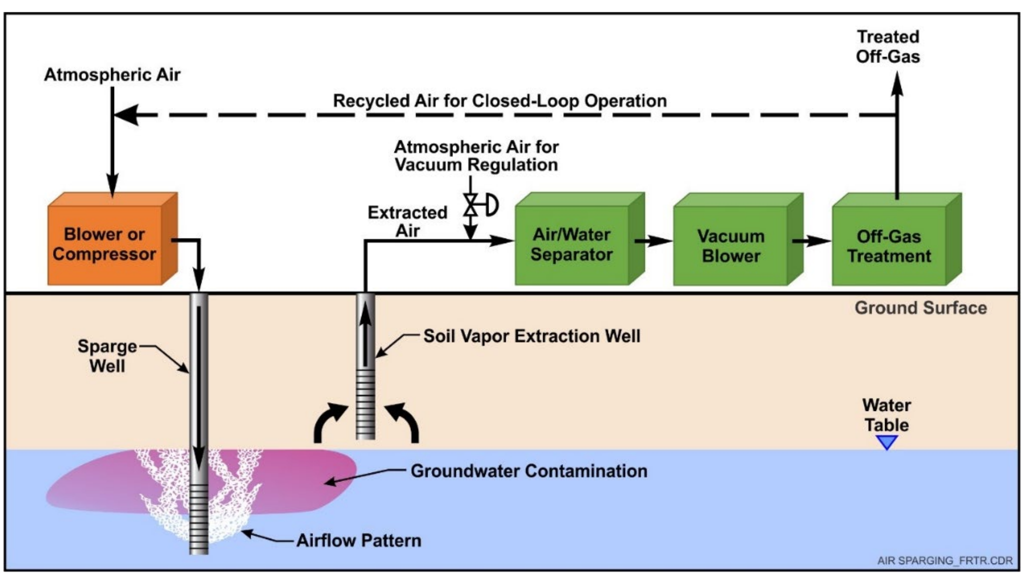


Figure 4-1. Typical Air Sparging System (FRTR, 2020)

4.2 Performance Plots

The performance of an AS system that is operated in conjunction with an SVE system should be assessed by plotting both the concentration of constituents in the extracted soil vapor and the amount of contaminant mass removed versus time. In addition, or in cases where a complementary SVE system is not operated, progress toward achieving cleanup objectives should be monitored by plotting the contaminant concentrations measured in groundwater samples collected from the performance monitoring wells versus time. An example of this type of performance plot is shown in Figure 4-2. All three types of plots will eventually exhibit asymptotic conditions as system performance declines and remediation progresses.

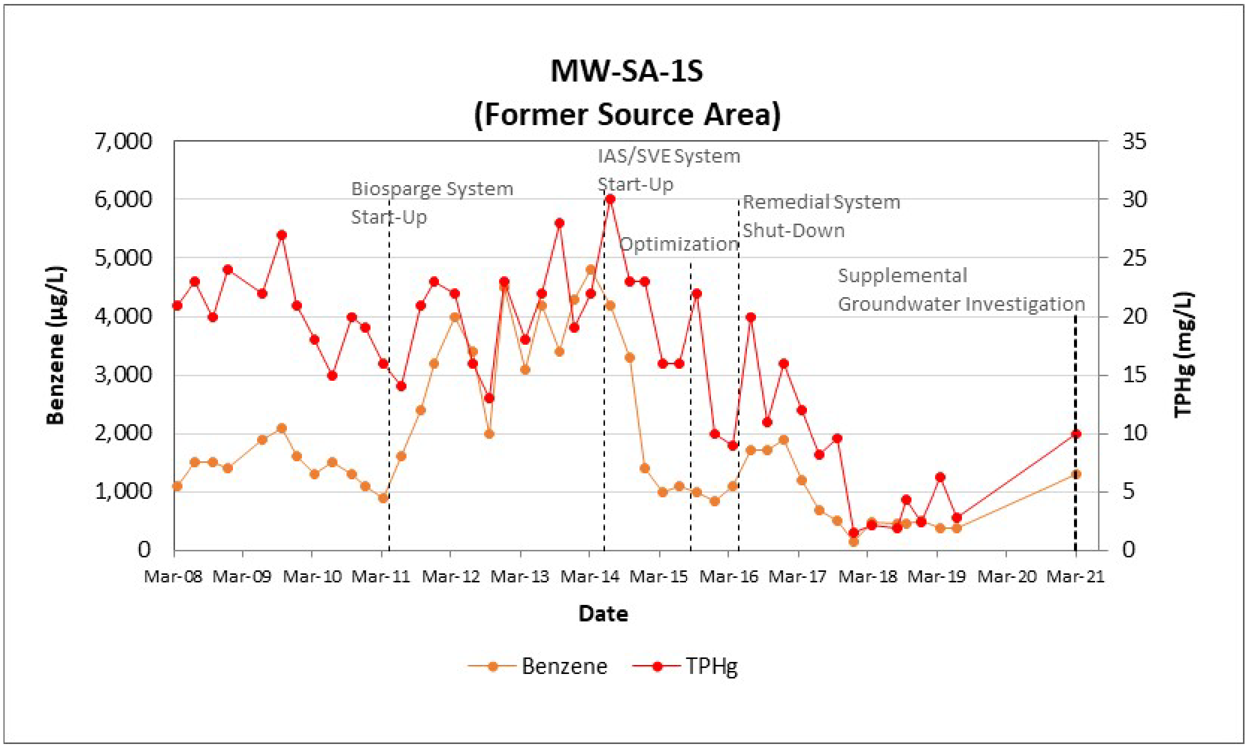


Figure 4-2. Concentration Trends for Total Petroleum Hydrocarbons, Gasoline Range (TPH-G) and Benzene, Moffett Field Site 14 South

Example: *After source area removal activities, long term monitoring was performed to track performance of the biosparge and AS/SVE remedial actions at Site 14 South, Moffett Field. The data demonstrated that contaminant of concern concentrations were significantly reduced as a result of optimizing a portion of the biosparge system installed in the former source area by transitioning to a more aggressive AS/SVE remedial system operation between 2014 and 2016. In 2016, fate and transport groundwater modeling suggested that final cleanup goals could be achieved via MNA, and the active remedial system was shut down. MNA sampling continued for four years, and a supplemental groundwater investigation was completed in 2021 to confirm that contaminant concentrations were adequately characterized throughout the site. Following remedial system optimization, system performance monitoring, and confirmation groundwater sampling, an evaluation of site-specific factors showed that the site was a candidate for closure under the California's Regional Water Quality Control Board's Low-Threat UST Case Closure*

Policy. This evaluation included verifying that that the groundwater was not suitable as a drinking water source. Several lines of evidence, including the reduction of contaminant concentrations over time (Figure 4-2) and additional statistical modeling were used to demonstrate that concentrations are stable or decreasing. This resulted in site closure and a no further action determination for the site from the regulatory agency in September 2022.

4.3 Common Operational Problems

A common issue encountered for AS systems is inadequate air distribution to all areas of the remediation target zone. Generally, this problem is due to an under-designed system, short-circuiting or unanticipated site conditions. Conversely, an AS system that is operating effectively will eventually reach a point at which the mass transfer of sorbed contaminants typically becomes desorption and/or diffusion-limited and asymptotic mass removal is observed. Table 4-1 lists some of the underlying causes of inadequate air distribution, as well as other problems that may affect the performance of AS systems.

4.4 Common Optimization Recommendations

When the various performance plots described in Section 4.2 depict asymptotic conditions, pulsing the system should be considered in an effort to restore a higher mass removal rate by producing new vapor flow pathways. More aggressive measures such as installing additional AS wells may also be evaluated. If asymptotic conditions persist after operational or system changes have been implemented, continued operation of the AS system will generally not result in the significant removal of additional mass. In this case, if further active remediation is necessary to address unacceptable risk remaining at the site, then implementing another technology should be evaluated. At low risk sites, MNA should be considered.

If the AS system is combined with SVE, a determination should be made if the air sparge vapors must continue to be actively collected by SVE. In cases where receptors are absent, there may be no risk in allowing the vapors to migrate up through the unsaturated zone and to escape to the atmosphere. In certain other cases, biological processes that operate in the unsaturated zone may consume aerobically degradable contaminants present in the vapor (e.g., biosparging). Table 4-1 provides additional guidance on optimizing AS system performance.

Example: *At NSB New London, an AS/SVE system at the Navy Exchange site reached contaminant concentrations in groundwater below remedial goals and asymptotic contaminant mass removal rates. Therefore, it was recommended that the system be shut down and post-remediation/rebound monitoring be initiated. If rebound in contaminant concentrations occurred, then pulsed operation of the AS/SVE system or biosparging was recommended.*

Table 4-1. Common Air Sparging System Operational Problems and Optimization Strategies

Operational Problem	Potential Causes	Potential Negative Impacts on Performance	Optimization Strategy
The zone of influence is insufficient or not as predicted.	• The permeability of the soil is lower than estimated. • Short-circuiting of air is occurring along the sparge well casings or subsurface utilities. • Heterogeneous soil is causing channeling of the injected air. • The water table is depressed due to seasonal fluctuations or drought conditions, resulting in sparge well screens being too shallow.	• The airflow may not contact some areas of contamination resulting in insufficient cleanup. • Cleanup will not be achieved or will take longer than estimated.	• Increase the airflow to the injection wells. • Install additional wells in the contaminated areas located outside the system's treatment zone. • Evaluate the system for evidence of short-circuiting; consider repairing, replacing, or relocating the affected wells. • "Pulse" operation of the injection wells to reduce short-circuiting through preferential pathways in the subsurface. • Evaluate screen zone depths compared to lowest water table conditions and consider installing deeper sparge wells if needed.
Increasingly high injection pressure is needed to maintain flow.	• The injection wells have been become plugged through mineral encrustation, biological fouling, or siltation.	• The airflow through the contaminated area will not be sufficient. • Cleanup will not be achieved or will take longer than estimated.	• Rehabilitate the affected wells with appropriate acids and/or biocides. • Redevelop the affected wells. • Replace the affected wells if rehabilitation or redevelopment is not possible.
The contaminant concentrations in the target zone are not decreasing as anticipated.	• The airflow through the contaminated area is not sufficient. • The airflow is short-circuiting. • An uncontrolled source area is present.	• Cleanup will not be achieved or will take longer than estimated due to an inability to supply air to all areas of the contaminated zone. • The presence of a continuing source will prevent achieving cleanup.	• Increase the airflow to the injection wells. • Install additional wells in the contaminated areas located outside the system's treatment zone. • Evaluate the system for evidence of short-circuiting; consider repairing, replacing, or relocating the affected wells. • Identify the potential source area and implement control measures. • Evaluate the use of alternate technologies including natural attenuation.
The contaminant concentrations in the target zone have reached asymptotic levels and/or rebound to higher levels when sparging is terminated.	• The removal of contaminants sorbed to the aquifer matrix is limited by site-specific desorption rates. • The removal of contaminants within low permeability zones is diffusion limited. • A continuing source is present.	• The slower rate of contaminant removal will extend cleanup time. • The presence of a continuing source will prevent achieving cleanup.	• "Pulse" operation of the injection wells to correspond to the contaminant desorption and/or diffusion rates. • Install additional wells in the contaminated areas. • Evaluate the use of alternate technologies including natural attenuation.

Table 4-1 (continued). Common Air Sparging System Operational Problems and Optimization Strategies

Operational Problem	Potential Causes	Potential Negative Impacts on Performance	Optimization Strategy
Sparging vapors are not properly controlled.	• Sparging is not operated in conjunction with an SVE system or the SVE system is not operating properly.	• Sparging vapors may accumulate in, or migrate to, undesirable areas.	• Ensure the sparge rate is not excessive. • Install an SVE system. • Optimize the performance of the SVE system.
Excessive groundwater mounding occurs.	• A low permeability zone causes air to be trapped in the sub-surface creating a local area of high piezometric levels.	• Contaminant migration may occur. • Overpressure may cause monitoring well caps to pop off.	• Decrease sparge flow rate. •"Pulse" the injection wells to reduce the mounding magnitude. • Install SVE or vent wells in zones to capture trapped air or allow it to vent to the surface.

5.0 BIOVENTING

5.1 System Description

Bioventing is a source reduction technology primarily used to treat vadose zone soils contaminated with petroleum hydrocarbons, but may also be applicable to other contaminants amendable to aerobic biodegradation. Bioventing works by introducing air into subsurface zones of contamination to simulate naturally occurring microorganisms to biodegrade the petroleum components (FRTR, 2020). Oxygen concentrations are increased to greater than 5 percent in the vadose zone by either extracting or injecting ambient air through a series of vent wells. In some deep bioventing applications, barometric pumping has been used to passively introduce air into the subsurface through changes in atmospheric and subsurface pressures. Unlike SVE or AS, the primary contaminant reduction mechanism in bioventing is biodegradation of contaminants, not extraction. Therefore, bioventing systems are operated at lower airflow rates than SVE or AS systems and can treat both volatile and non-volatile petroleum hydrocarbons. In addition to the induced airflow, nutrients are sometimes also injected into the subsurface to facilitate microbial growth in nutrient-deficient soil. Biodegradation is an inherently slow process such that the systems are used with the understanding that operation may continue for several years to reach cleanup objectives. However, because it is simple and relatively inexpensive to use, bioventing is often the remedial technology selected for sites where historical practices have resulted in releases of various fuels.

Figure 5-1 illustrates a typical bioventing system utilizing injection to induce airflow. The primary components are identical to those used in SVE and include injection/extraction wells, piping, and a blower. Soil-gas monitoring points typically are installed above the water table at several locations at the site. They are used to measure changes in concentrations of oxygen and carbon dioxide in soil gas, which in turn are used to calculate biodegradation rates. Off-gas treatment is usually not required (in the case of an extraction system[1]) unless contaminant concentrations in the extracted vapor exceed allowable limits. The bioventing system may also incorporate one or more nutrient addition wells or trenches if microbial growth is limited by a deficiency in naturally occurring nutrients.

5.2 Performance Plots

Common operation and monitoring data collected to evaluate the effectiveness and efficiency of bioventing systems includes the following:

- Subsurface vacuum measurements at soil gas VMPs.
- Oxygen distribution in the vadose zone.
- Soil gas monitoring for carbon dioxide and methane in the vadose zone.
- Extracted vapor flow rates and contaminant concentrations.
- Water table measurements.

[1] Injection systems can result in lower cost since a vapor stream, which may require treatment, is not generated. However, vapor intrusion into nearby buildings is a concern using an injection system due to the elevated pressures and flowrates generated during operation.

Because bioventing systems may reduce contaminant mass through volatilization and biodegradation, both mechanisms should be monitored to measure total mass reduction. Contaminant mass extracted can be estimated from the extracted vapor flow rate and the concentration of VOCs measured in the extracted vapor. The mass of contaminants that is biologically degraded can be interpreted from oxygen concentrations measured in soil gas respirometry tests, preferably, at VMPs, or in the extracted vapor itself. Pressure or vacuum isopleth maps can be prepared to determine if the vacuum distribution is consistent with design expectations and to demonstrate that adequate oxygen delivery is occurring in the treatment zone. Carbon dioxide concentration may also be measured; however, it is not always a reliable indicator of aerobic biodegradation due to adsorption to soil moisture and buffering in alkaline soil. Performance monitoring of bioventing systems utilizing only injection wells is limited by an inability to collect extracted vapor, although this can be addressed by installing separate soil gas monitoring points in the treatment area. Figure 5-2 shows a performance plot for a typical bioventing system. The figure illustrates that the system has achieved asymptotic levels with respect to VOC and carbon dioxide concentrations. The figure also shows that cumulative mass removed and degraded has similarly reached an asymptotic level.

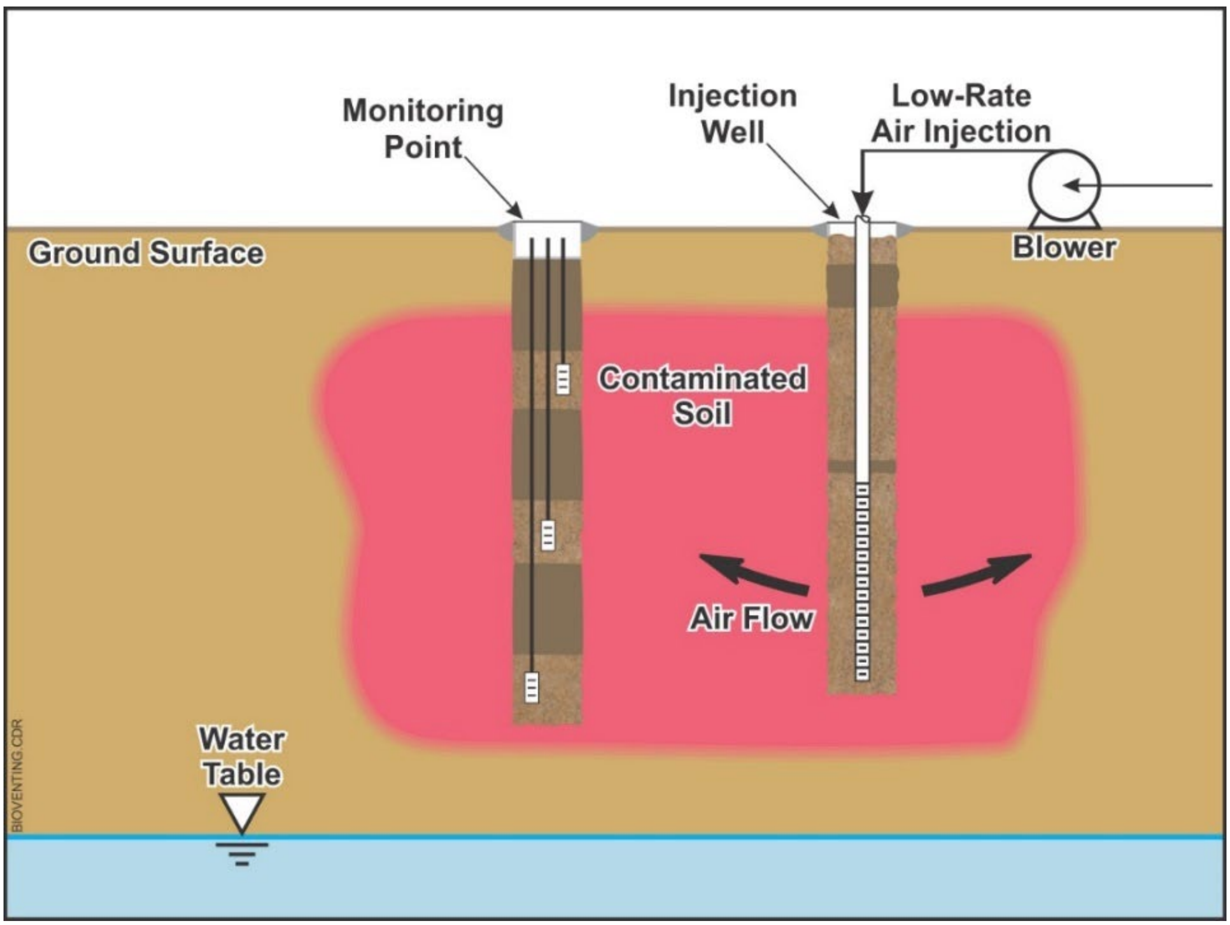


Figure 5-1. Typical Bioventing System (FRTR, 2020)

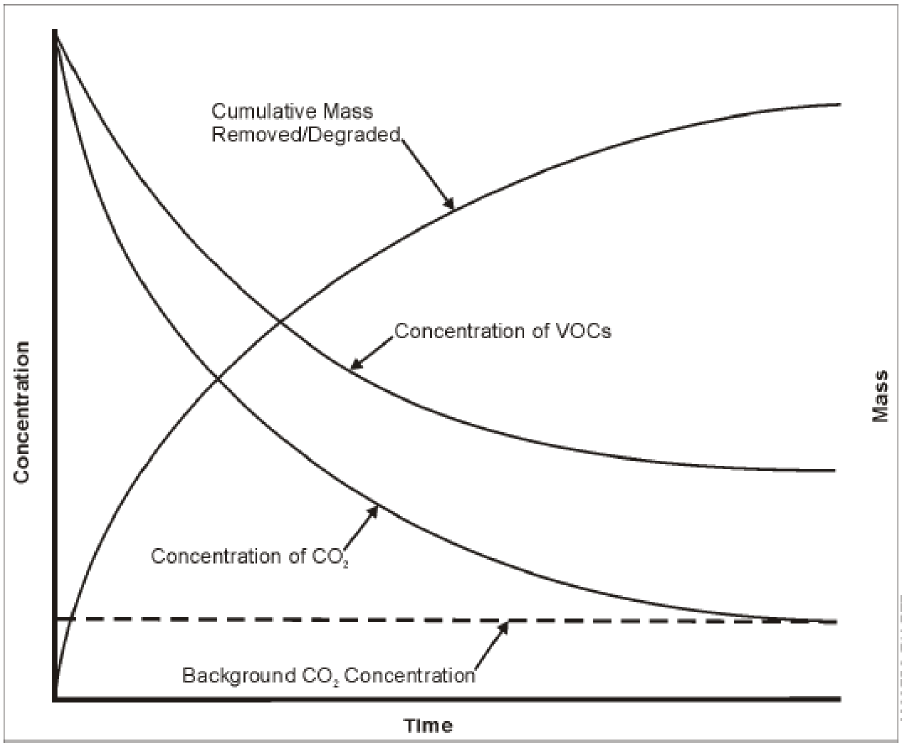


Figure 5-2. Performance Plot of a Typical Bioventing System

5.3 Common Operational Problems

Two conditions must be met for bioventing to be successful. First, an adequate population of microbes must be present to sustain biodegradation. A natural population of these microbes is found at a majority of sites. Second, sufficient air must flow through the treatment zone to maintain aerobic conditions. As in the case of SVE systems, bioventing performance problems are commonly related to an inability of a system to induce airflow to all areas of the remediation target zone. Occasionally, other site conditions may be only marginally suited to support efficient biodegradation, a situation that underscores the need for adequate bench and/or pilot-scale testing. Table 5-1 lists these and other problems common to bioventing systems.

5.4 Common Optimization Strategies

Bioventing systems should be made as simple as possible to run continuously with little operator attention. Automatic dial-out equipment to notify operators of unplanned shutdowns is a convenient way to reduce the expense of routine system checks, and to optimize system up time. To optimize a bioventing system, system parameters are typically recorded weekly or biweekly and a review of the system performance should be conducted at a minimum of every 6 months. In-situ respiration tests should be performed at all injection or extraction wells and at soil VMPs to assess microbial activity if cleanup is taking longer than anticipated. Soil gas samples collected from these locations are typically analyzed for carbon dioxide, oxygen, and TPH. This testing and sampling are to be used for assessing remedial progress and to ensure that biodegradation is continuing.

When asymptotic conditions for the constituents of concern and oxygen are first established in VMPs and extracted vapor, if applicable, alternative steps such as initially increasing the airflow rate should be explored in an effort to restore a higher degradation rate. Subsequently, the airflow may be pulsed when asymptotic conditions are re-established. Should asymptotic levels persist despite the modifications, continued operation of the bioventing system will generally not produce additional reduction in the concentration of the constituents. In this case, if further remediation is necessary, implementing either another technology or MNA should be considered. However, when the high-risk constituents (e.g., benzene) have been degraded, a case should be made to decommission the system and pursue site closeout. Table 5-1 provides additional guidance on bioventing system operation and optimization.

Table 5-1. Common Bioventing System Operational Problems and Optimization Strategies

Operational Problem	Potential Causes	Potential Negative Impacts on Performance	Optimization Strategy
The design radius of influence has never been achieved in individual wells and oxygen concentrations are not increased above 5 percent throughout the treatment zone.	• The air permeability of the soil is lower than estimated. • Short-circuiting is occurring due to the presence of preferential flow paths. • The vent wells have been incorrectly designed or installed, or placed too far apart. • The blower is improperly sized.	• The contaminants located outside the effective radius of the bioventing are not biodegraded and prevent reaching cleanup goals. • The oxygen concentrations are not increased above 5 percent, resulting in low biodegradation rates that increases cleanup time.	• Perform a subsurface investigation to further characterize the soil permeability and the preferential flow paths. • Install additional vent wells in the contaminated areas located outside the system's treatment zone. • Replace incorrectly designed or installed wells. • Resize the blower.
The contaminant concentrations have been reduced at some but not all wells.	• Treatment may be complete in some areas of the site. • The airflow to some areas of the site is inadequate. • Surface irrigation limits effectiveness of air distribution in the vadose zone.	• Continued operation of nonproductive wells will not be cost effective. • The low airflow rates will limit mass reduction and increase cleanup time. • Oxygen concentrations are not increased above 5 percent throughout the treatment zone, resulting in inadequate treatment.	• Adjust injection/extraction rates at wells to balance air flow throughout the treatment zone and establish oxygen concentrations above 5 percent to support biodegradation of contaminants. • Install additional vent wells in the areas where airflow is not adequate. • If oxygen concentrations are high and contaminant concentrations are not reduced, perform respiration tests to determine the degradation rate. Evaluate the need for nutrient and/or moisture addition or other bioaugmentation to increase degradation rates. • Move or terminate irrigation system.
The contaminant concentrations in soil gas samples have reached asymptotic levels.	• The reduction of contaminants sorbed to the soil is limited by site-specific desorption rates. • The reduction of contaminants within low permeability zones (tight soil layers) is diffusion limited. • The vent wells are not properly located or screened to treat all contaminated areas. • An uncontrolled source area continues to release contaminants.	• The slower rate of contaminant mass reduction due to desorption/diffusion limitations will extend cleanup time. • The presence of a continuing source of contaminants will prevent cleanup.	• "Pulse" the wells or reduce airflow rates to correspond to contaminant desorption and/or diffusion rates. • Install additional wells in the contaminated areas located outside the system's treatment zone. • Install wells with screens isolated to the depths with highest contaminant concentrations remaining, as identified through discrete depth sampling at soil gas VMPs. • Implement an alternative technology such as source control including MPE or excavation, if feasible.

Table 5-1 (continued). Common Bioventing System Operational Problems and Optimization Strategies

Operational Problem	Potential Causes	Potential Negative Impacts on Performance	Optimization Strategy
			• Evaluate alternate technologies such as thermally-enhanced SVE or bioventing for petroleum-related contamination.
Low concentrations of contaminants are measured during operation, but high concentrations reappear when the system is shut off.	• The reduction of contaminants sorbed to the soil is limited by site-specific desorption rates. • The reduction of contaminants within low permeability zones (tight soil layers) is diffusion limited. • The airflow rate is higher than necessary due to desorption and diffusion limits. • The airflow is short-circuiting due to preferential flow.	• The slower rate of contaminant mass reduction due to desorption/diffusion limitations or preferential flow paths will extend the cleanup time.	• "Pulse" the wells or reduce the airflow rates to correspond to contaminant desorption and/or diffusion rates. • Temporarily shut off the system and perform equilibrium testing at vapor monitoring points to identify the more highly contaminated areas where SVE should be focused. • Identify and excavate any desorption/diffusion-limited hot spots, if feasible. • Evaluate alternate technologies such as thermally-enhanced SVE or bioventing for petroleum-related contamination.
The contaminant concentrations in vapor monitoring points remain high despite high mass reduction rates.	• An uncontrolled source area or free product may be present. • Vapor flow may be short-circuiting away from monitoring points.	• The presence of a continuing source of contaminants will preclude cleanup. • The contaminants located outside the effective radius of the vacuum are not removed and prevent reaching cleanup goals.	• Perform further subsurface investigation to identify additional source areas and potential free product. • Identify and control any source areas including excavation, if feasible. • Install additional vent wells in the areas where airflow is not adequate.
The system extracts high volumes of water.	• The well screens are installed too close to the water table causing upwelling to occur.	• Water table upwelling may occlude well screens causing lower mass reduction that extends cleanup time. • The extraction of high volumes of water may result in excessive system downtime.	• Replace the existing wells with shallower vertical wells or with horizontal wells. • Change from extraction to injection bioventing operation. • Consider temporarily shutting down the system during periods of seasonal high water table. • Evaluate the use of an alternate technology that is not influenced by a high water table.
Water is recovered in the monitoring points.	• The monitoring point screens are installed too close to the water table causing upwelling to occur.	• Will preclude the ability to collect a vapor sample. • The accuracy of the data may be compromised.	• Develop a detailed CSM. Ensure understanding of site conditions. • Redesign and install soil gas monitoring points.

6.0 MULTI-PHASE EXTRACTION

6.1 System Description

MPE is a technology designed to simultaneously remove any combination of light non-aqueous phase liquid (LNAPL), groundwater, and vapor. Treatment by MPE targets remediation of the vadose (or unsaturated) zone, as well as the difficult to treat capillary/smear zone and shallow saturated zone where a large percentage of residual contaminant mass and LNAPL often accumulates (FRTR, 2020). The MPE system pulls a vacuum on a recovery (or extraction) well to create a pressure gradient that promotes movement of LNAPL into the well and treats the vadose zone at the same time by increasing the oxygen levels in the unsaturated soil through soil-gas extraction. The system can be designed to withdraw groundwater, free product, and soil gas in one process stream using a single above ground pump and a tube positioned in each well so that the end of the tube is near the water-table level in the formation (Figure 6-1). Alternatively, individual down-well pumps can be positioned in each well to recover the LNAPL and groundwater, while using a single above ground pump to generate the vacuum in the recovery wells and remove vapor. The extracted oil/water mixture is separated into LNAPL and water, then the water is treated if necessary, and discharged in accordance with local regulations. LNAPL is recovered and recycled. Soil gas vapor is treated if necessary and discharged into the atmosphere.

LNAPL and groundwater are removed from the well by air entrainment. The depth of the recovery tubes (or pumps) can be adjusted manually, if needed. Systems can be designed to generate a vacuum of up to about 20 inches mercury (Hg) on the recovery well, which creates the pressure gradient to force movement of LNAPL into the well. The negative pressure established in the well depends on the air withdrawal rate and the permeability of the surrounding formation. As vapor is removed from the formation, ambient air is drawn into the subsurface replenishing the oxygen in the formation. Hence, biological degradation of the petroleum hydrocarbons or other chemicals of potential concern (COPCs) will be enhanced. The MPE system cycles between recovering liquid (free product and/or groundwater) and soil gas. The rate of soil gas extraction is dependent on the recovery rate of liquid into the well, the screened interval of the well, and the permeability of the formation. When free-product removal activities are complete, the MPE system can be converted to a conventional bioventing system to complete remediation of the unsaturated zone soils if necessary.

MPE is used primarily to recover LNAPL and can help to remediate VOCs and SVOCs in the unsaturated zone. The treatment of LNAPL-contaminated soils using MPE technology offers the following advantages:

- Greater LNAPL recovery rates are achieved compared to conventional methods.
- A single above ground pump may be used to extract fluids from multiple wells, which may result in lower capital costs at large sites compared to conventional pump-and-treat technologies.
- Dissolved and emulsified hydrocarbons are recovered in the extracted groundwater.
- VOCs and SVOCs are recovered from the vadose zone through soil vapor extraction.

- Biodegradation of hydrocarbons in the vadose zone is stimulated through the introduction of fresh air into the subsurface.

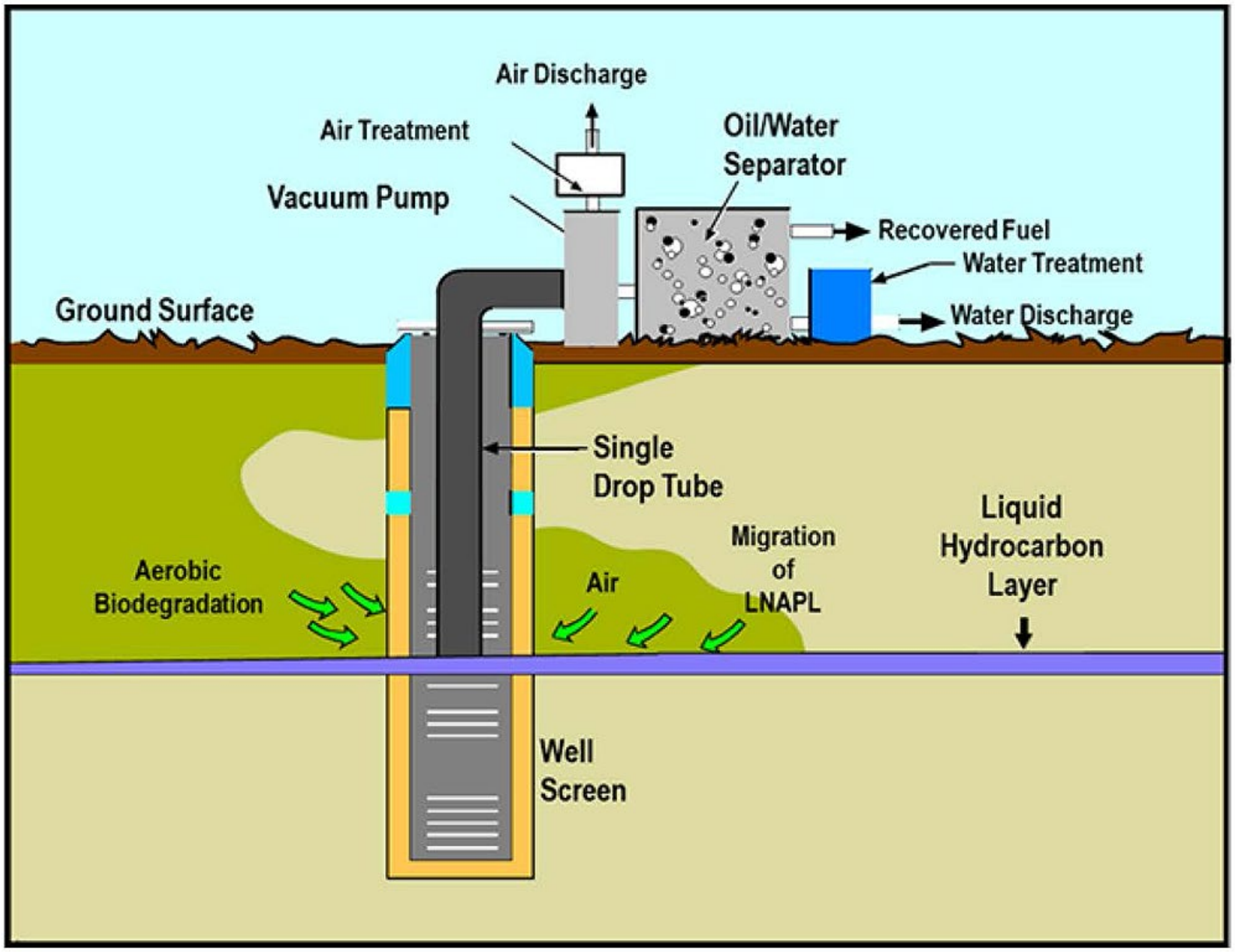


Figure 6-1. Typical Multi-Phase Extraction System (FRTR, 2020)

As with any treatment technology there are several limitations associated with MPE. These include:

- Off-gas treatment may be required depending on the type of LNAPL contamination, degree of weathering, and regulatory requirements.
- Water treatment may be required due to the formation of oil-water emulsions.
- Channeling may occur in the subsurface.
- As with all P&T technologies, it is not possible to remove all of the LNAPL in the subsurface. A residual thin layer of LNAPL periodically may be observed in the extraction wells.

Many times treatment is required for the aqueous and vapor streams that are generated by the MPE system. A number of technologies are available for each. Selection of a particular technology should be based on site-specific conditions including concentrations of hydrocarbons in each of the streams, presence of emulsion in the aqueous phase, available infrastructure at the site, noise ordinances, etc. For the aqueous stream, granular activated carbon (GAC) is commonly used if the concentration in the aqueous phase is relatively low since the cost effectiveness of GAC decreases as mass loading of the hydrocarbons increase. Vessels of hydrophobic organic clay media are commonly used to pretreat the water to remove emulsified oils before pumping the water through the GAC. Alternatively, for water that contains very high concentrations of hydrocarbons, chemical treatment that includes the addition of coagulants and flocculants combined with dissolved air flotation may be considered. Treated groundwater may be discharged to the surface, to a wastewater treatment plant (WWTP), or reinjected back into the aquifer. Note that if water will be pumped to a WWTP, very little if any pretreatment of the process water may be required.

Local regulations may allow the vapor stream to be discharged directly to the atmosphere without any type of treatment depending on the mass loading of hydrocarbons in the stream. However, in most cases, some form of pretreatment will be required. Similar to the aqueous stream, low concentrations of hydrocarbons in the vapor stream, typically less than a few hundred parts per million, may be treated using GAC. Higher concentrations can be treated using vapor phase GAC; however, the cost may become prohibitive. Common options for treating high concentrations include thermal and catalytic oxidizers, and internal combustion engines.

6.2 Performance Plots

Plotting the vapor and water flow rates is useful in determining when steady-state conditions have been reached in the subsurface (Figure 6-2). Once such conditions occur, it is possible to quantify system performance in terms of mass removal rates and unit mass removal cost.

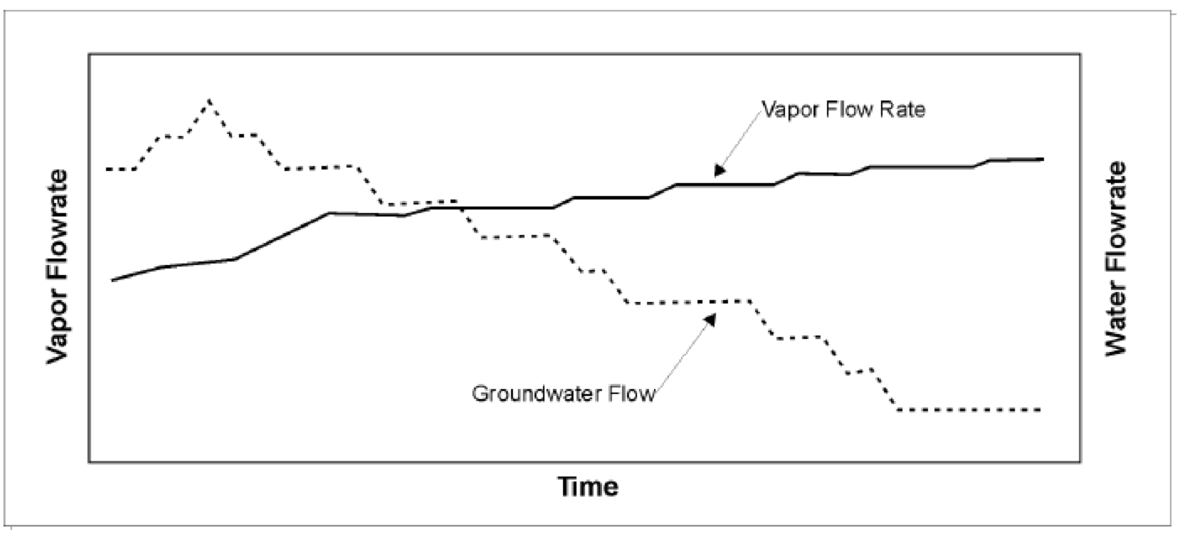


Figure 6-2. Performance Plot of a Typical Multi-phase Extraction System

Performance should be gauged based on changes in rate of recovery of hydrocarbons. Hydrocarbon recovery as LNAPL, in the vapor phase and in the aqueous phase should all be monitored. As shown in Figure 6-3, a large percentage of the hydrocarbons will be recovered during the first several months of operation and eventually recovery will approach an asymptotic value. A decline curve analysis (Figure 6-4), which plots the volume of LNAPL recovered during a time interval as a function of the average recovery rate during that interval is a useful tool for predicting the total volume of LNAPL that will be recovered by the time that the recovery rate decreases to a given value.

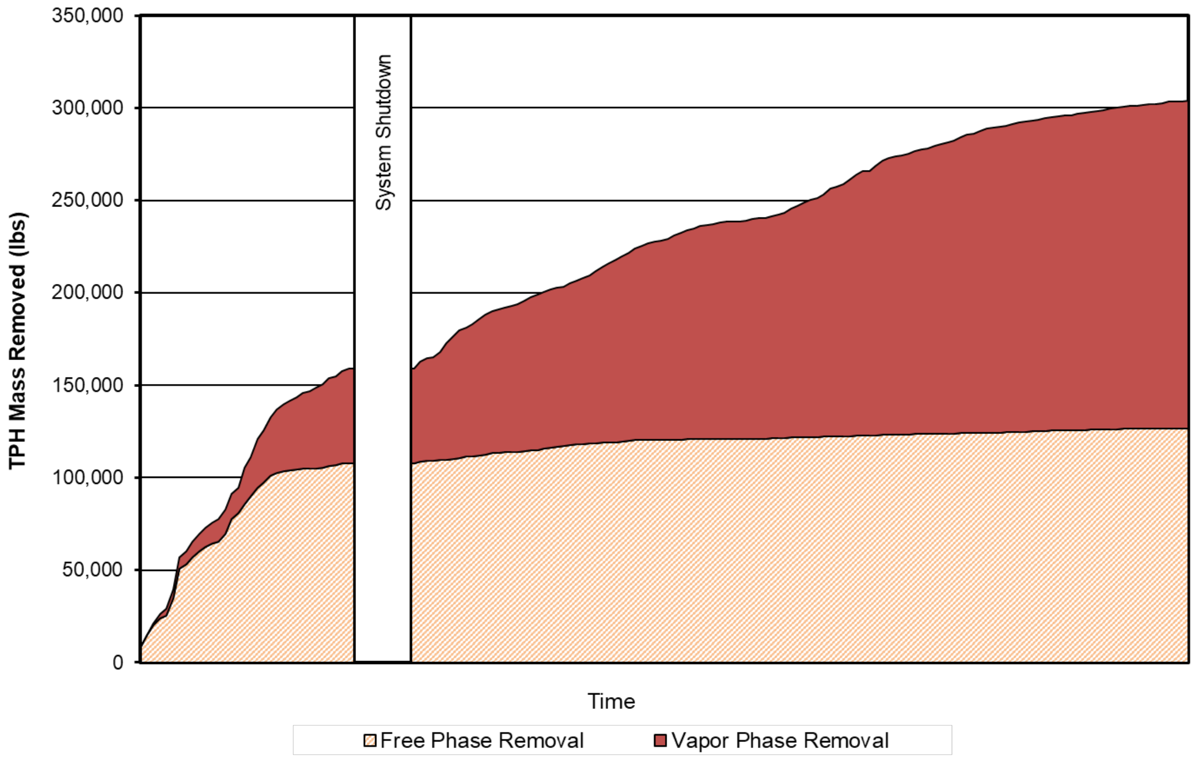


Figure 6-3. Cumulative Mass of Hydrocarbons Removed

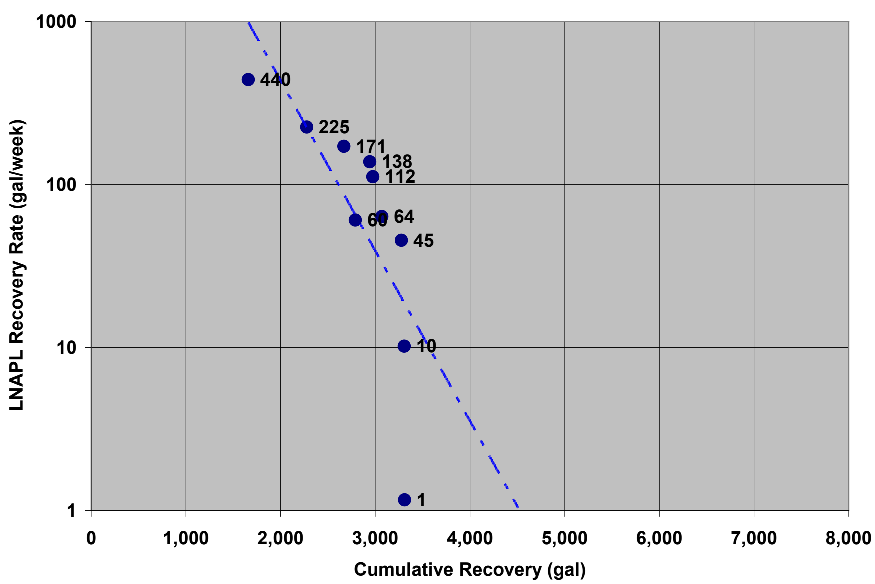


Figure 6-4. Decline Curve Analysis

6.3 Common Operational Problems

As with most technologies in which fluids are recovered from the aquifer, operational problems focus around the inability to achieve the design radius of influence due to heterogeneities in the subsurface and short-circuiting. In addition, because MPE systems recover three phases (LNAPL, groundwater, and vapor), challenges and high costs associated with separating and treating these streams are common. Table 6-1 summarizes operational problems that are typical of MPE systems.

6.4 Common Optimization Strategies

Practical application of free product recovery systems has shown that even under favorable site conditions only a small percentage of the total product released can ever be recovered. Therefore, it is prudent to have established criteria for suspending free product recovery to avoid needless, nonproductive operation of the system. A multiple lines of evidence approach should be used that demonstrates that: 1) the LNAPL is not migrating and doesn't pose a threat of additional contamination of surface water or groundwater, 2) LNAPL presents no risk to human health or the environment under current and reasonably anticipated future scenarios, and 3) LNAPL recovery has been completed to the maximum extent practicable taking into consideration LNAPL transmissivity data. The first two lines of evidence can be demonstrated through various modeling and risk assessment techniques, which are not directly related to operation and optimization of the MPE system and are described elsewhere in the literature. The third line of evidence is best demonstrated by documenting the diminishing recovery of LNAPL, decreased recovery of hydrocarbons in the aqueous and vapor phase, increased cost per mass LNAPL recovered, and reduced transmissivity of remaining LNAPL. These topics are further discussed in the *NAVFAC LNAPL Site Management Handbook* (NAVFAC, 2010) and the *New Developments in LNAPL Site Management* fact sheet (NAVFAC, 2017b).

Tracking the incremental costs of removing each additional unit of contaminant mass is a good indicator of MPE system efficiency, and a means of illustrating that the system has reached the practical economic limits of its usefulness. The incremental cost per pound of operating MPE systems can be reduced by either decreasing the operating cost or increasing the mass removal rate. Adjustments should be made in both of these areas to maximize the cost-effectiveness of the remedial action and to satisfy regulatory criteria for accomplishing the site cleanup.

Optimizing the operation of the MPE system requires that reliable data be collected on a routine basis to track extraction rates for the system as a whole and possibly the extraction rates of each individual well. The types of information that should be collected include:

- Concentration of contaminants extracted in liquid and vapor streams.
- Thickness of LNAPL and groundwater elevation in each monitoring well before and after operation.
- An estimation of transmissivity (i.e., recoverability and migration) based on MPE system recovery data or other baildown test data.
- Total system vacuum and individual well vacuums.
- Liquid flow rates (LNAPL and water) for the overall system.

- The vacuum radius of influence from vacuum monitoring points.
- The hydraulic radius of influence from water levels in monitoring wells.

When the rate of mass removal first reaches asymptotic conditions, alternative steps such as pulsing or operating at a lower, sustained extraction rate should be explored in an effort to restore a higher mass removal rate. If plume migration is a concern, any measures adopted should ensure that hydraulic containment is maintained. Should asymptotic levels persist despite operational or system changes, continued operation of the MPE system will generally not produce additional reduction in the concentration of the constituents. In this case, if further remediation is necessary, implementing either another technology or NSZD should be considered. Table 6-1 provides additional guidance on optimizing MPE system operations. Certain recommendations applicable to optimizing pump and treat and SVE systems are also applicable to MPE systems.

Example: *At Naval Air Weapons Station (NAWS) China Lake, California, free product recovery was optimized by adding free product skimmers to monitoring wells where increased LNAPL was observed within the radius of influence of the vacuum-enhanced skimming system. Over time, LNAPL recovery rates again reached asymptotic levels after optimization efforts. Additional data were collected, including LNAPL transmissivity, carbon dioxide flux measurements, and subsurface temperature readings to evaluate NSZD as an alternative to the on-going active treatment.*

Any equipment used to treat the liquid and vapor treatment systems should be optimized throughout the life cycle of the MPE system. Concentrations of hydrocarbon constituents in both the liquid and vapor streams typically are very high during the first several months of operation but will decrease significantly shortly thereafter. Hence, it may be appropriate to use a very aggressive treatment approach such as chemical treatment for the aqueous phase or thermal oxidation for the vapor phase, but as concentrations decrease, these methods can be replaced by less costly alternatives (such as GAC). In addition, constant optimization of these systems is required to compensate for changes in loadings in the effluent streams. For instance, as concentrations in the MPE effluent streams decrease, GAC may last longer and in the case of chemical treatment, the required mass of coagulants and flocculants will be less. Conversely, as concentrations in the vapor stream decrease, additional auxiliary fuel would be required to operate a catalytic oxidizer; hence, the operating cost will increase. A flexible design is key to allowing treatment to be modified or transitioned to optimize performance and cost.

Table 6-1. Common Multi-Phase Extraction System Operational Problems and Optimization Strategies

Operational Problem	Potential Causes	Potential Negative Impacts on Performance	Optimization Strategy
The radius of influence is insufficient or not as predicted.	• The air permeability of the soil is lower than estimated. • Short-circuiting is occurring due to the presence of preferential flow paths. • The extraction wells or drop tube depths have been incorrectly designed or installed.	• The lower LNAPL and contaminant mass removal rates results in incomplete remediation and increased remediation time. • Contaminants located outside the effective radius of the vacuum are not removed and preclude reaching cleanup goals. • The number of pore volumes of soil gas exchanged in the contaminated area is limited and results in low mass removal that increases cleanup time.	• Perform a subsurface investigation to further characterize the soil permeability and preferential flow paths. • Install additional wells in the contaminated areas located outside the system's treatment zone. • Replace the incorrectly designed or installed wells. • Adjust drop tube depths to target the LNAPL-water interface in each extraction well to maximize LNAPL mass removal rates. • Evaluate vacuum pump sizing/capacity.
The vacuum levels are decreasing and the airflow rate is increasing.	• Short-circuiting is occurring due to preferential flow paths. • Short-circuiting is occurring through shallow or improperly sealed wells.	• A lower rate of mass removal in the vapor phase will result in incomplete remediation or increased remediation time.	• Evaluate the system for evidence of short-circuiting; consider repairing, replacing, or relocating the affected wells. • Install a surface seal.
The LNAPL thickness and contaminant concentrations remain high despite high mass removal rates.	• An uncontrolled source area is present.	• The presence of a continuing source of contaminants will prevent cleanup.	• Perform further subsurface investigation to identify additional source areas and potential free product. • Identify and control source areas including excavation, if feasible.
The LNAPL or contaminant plume is migrating.	• Drop tube depths are not aligned with the LNAPL-water interface. • The groundwater extraction rate is insufficient to establish a capture zone. • The system is subject to prolonged shut down. • The number of extraction wells is inadequate, or they are improperly located.	• Failure to maintain hydraulic containment will allow the plume to enlarge in size and potentially reach receptors. The larger area of contamination will also result in increased remediation time and require expanding the remediation system.	• Adjust drop tube depths to target the oil-water interface in each extraction well to maximize LNAPL mass removal rates and reduce the potential for LNAPL migration. • Increase the groundwater extraction rate. • Increase the system uptime through a preventive maintenance program. • Install additional wells, as necessary. • Evaluate other remedial technologies.
The LNAPL to water ratio is decreasing, but LNAPL remains in the treatment area.	• Drop tube depths are not aligned with the LNAPL-water interface. • Low LNAPL transmissivity is limiting the effectiveness of MPE treatment.	• Above ground treatment costs increase due to the larger percentage and volume of water being extracted. • The lower LNAPL removal rate results in increased remediation time and increased cost.	• Adjust drop tube depths to target the LNAPL-water interface in each extraction well and maximize LNAPL mass removal rates.

Table 6-1 (continued). Common Multi-Phase Extraction System Operational Problems and Optimization Strategies

Operational Problem	Potential Causes	Potential Negative Impacts on Performance	Optimization Strategy
			• Evaluate skimming or other passive LNAPL recovery alternatives if transmissivity remains greater than 0.8 ft^2/day.
Emulsion is formed in the process water.	• High shear mixing of LNAPL and groundwater. • Commonly occurs at sites that contain diesel and heavier fuels and at sites where surfactants may have been in use.	• High water treatment cost.	• Separate the LNAPL from the water at the recovery wells (in-well separation). • Minimize pumping of liquids and lengths of manifold.
Water and/or vapor treatment are cost prohibitive.	• Improperly designed system.	• Pre-maturely discontinuing operation and transitioning to a less aggressive technology. Extended cleanup time can result.	• Use a treatment train approach. Transition from a more costly aggressive treatment technology used when loadings in water or vapor stream is high to a less costly technology as loadings decrease over time. • Revisit system design.
Hydrocarbon recovery as LNAPL reaches asymptotic levels, but LNAPL thickness in site wells is greater than the regulatory expectation for recovery to the "maximum extent practicable."	• The number of extraction wells is inadequate, or they are improperly located. • Drop tube depths are not aligned with the LNAPL-water interface. • The LNAPL transmissivity is low, limiting the ability to recover remaining LNAPL. • For the same LNAPL in-well thickness, the volume of LNAPL per unit area of the formation can be different. In-well LNAPL thicknesses in monitoring wells vary with changes in groundwater elevations.	• The continued operation of non-productive wells is not cost effective.	• Ensure that drop tube depths are low enough to extract remaining LNAPL. Adjust drop tube depths to target the LNAPL-water interface in each extraction well. • Evaluate other technologies if mass removal remains high in the vapor and/or liquid phases. • Evaluate skimming or other passive LNAPL recovery alternatives if transmissivity remains greater than 0.8 ft^2/day. • Evaluate the need to install additional wells in areas with high levels of contamination located outside the system's treatment zone. • Evaluate NSZD at low risk sites where LNAPL is not mobile.

7.0 FREE PRODUCT RECOVERY

7.1 System Description

At sites where there has been a release of hydrocarbon (petroleum) products, it is usually necessary to recover free-phase petroleum that is found above the water table. Free product recovery consists of several technologies ranging from simple hand bailers and passive skimmer systems to more complex active skimming systems and large-scale total fluids recovery systems (FRTR, 2020). Most petroleum cleanup regulations require the removal of free-phase liquid prior to or concurrent with implementing other soil and groundwater remediation systems. The remedial objective of free product recovery is to remove the liquid-phase contamination as quickly as possible to prevent continued contamination of the surrounding soil and groundwater. The various methods used to accomplish this are collectively known as free-phase product recovery.

Different techniques are used to recover free-phase petroleum product. Under shallow water table conditions, trench systems may be used to intercept and collect the free product as it migrates along the capillary fringe. Under deeper water table conditions, recovery wells screened across the water table can be used to recover free product. A wide variety of pumps may be used in the trenches and wells. Total fluids pumps establish a cone of depression and remove both free product and groundwater. Other pumps “skim” the free product from above the water table without pumping groundwater. These pumps may be used alone or in combination with water table depression pumps that are installed below the free product lens to remove groundwater and establish a cone of depression. Components of a typical free product recovery system include wells or trenches, pumping equipment, transfer piping, separation equipment, and liquid treatment units. Figure 7-1 is an illustration of a free product recovery system showing both a recovery well and interceptor trench.

Another technique, known as MPE, utilizes a vacuum to recover the free phase petroleum product. MPE combines vacuum extraction with bioventing to remove free product and to stimulate the aerobic biodegradation of petroleum contaminated soil in the unsaturated zone, respectively. Additional information regarding MPE is provided in Section 6.

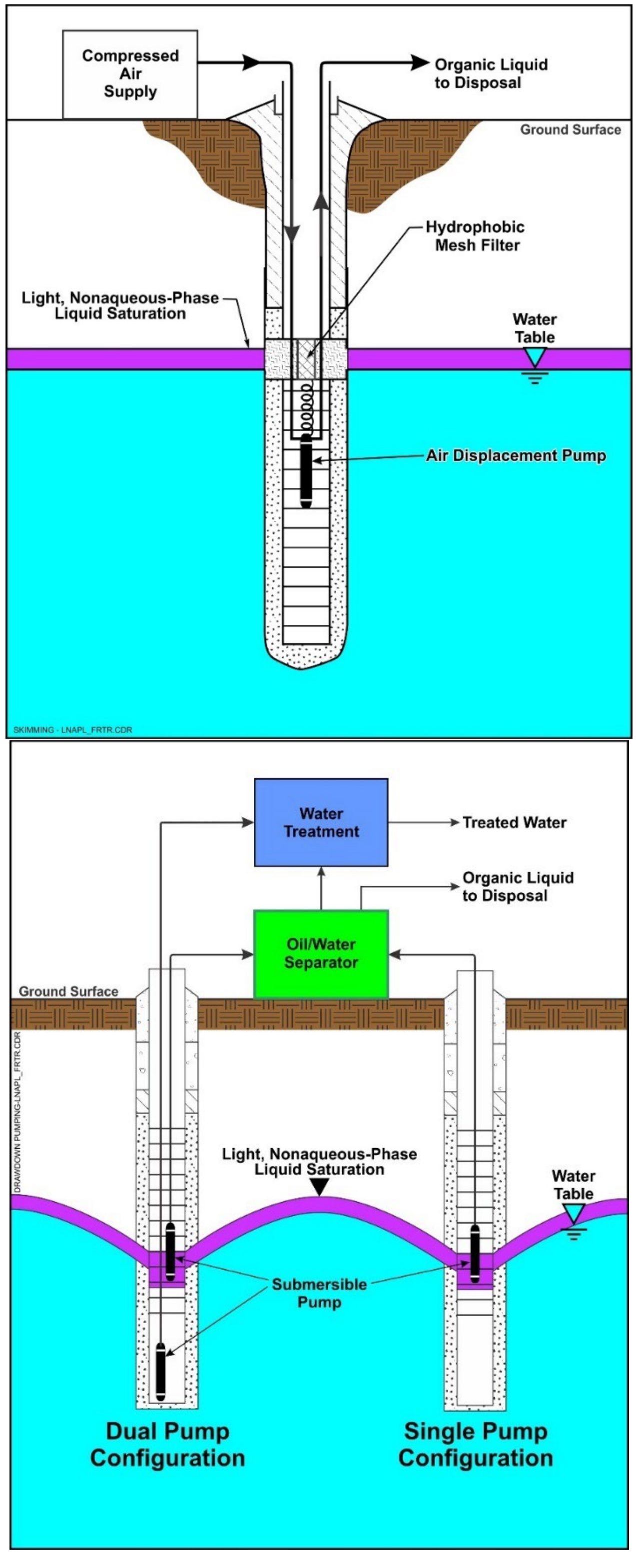


Figure 7-1. Skimming and Dual/Single Pump Free Product Recovery Systems (FRTR, 2020)

7.2 Performance Plots

Figure 7-2 shows a performance plot for a free product recovery system. The plot illustrates the asymptotic behavior that is typical of the recovery rate for this type of system. Initially, product recovery is relatively rapid but soon decreases as the amount of recoverable free product is diminished.

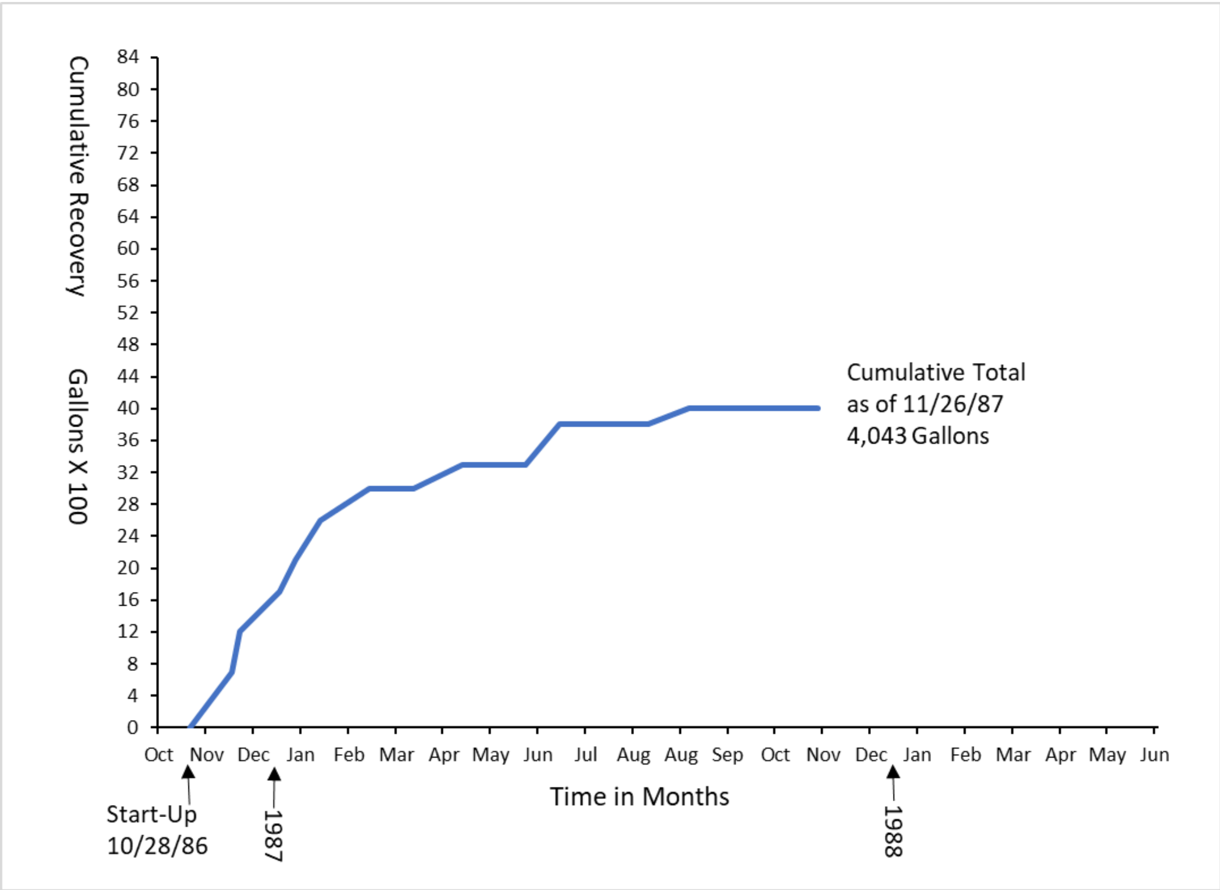


Figure 7-2. Performance Plot of Free Product Recovery System at Marine Corps Air Station (MCAS) New River

Example: *The system represented in Figure 7-2 was installed at MCAS New River, North Carolina, following the discovery of a release from a JP-5 line. The system, which was installed as an interim measure, operated for 1 year and recovered over 4,000 gallons of product. Of the total fuel volume recovered by the interim system, approximately 70% of the product was recovered in the first quarter of operation. Eighty-five percent was removed through the second quarter and nearly 100% of the total volume was removed by the end of the third quarter.*

7.3 Common Operational Problems

Table 7-1 lists operational problems common to free product recovery systems. Many of the problems listed are related to the general operation and maintenance of the recovery wells and pumps. Table 6-1 lists operational problems specific to MPE systems. Depending on the free product recovery technique used, problems included in Tables 2-1 (P&T system) and 5-1 (bioventing system) may also be applicable to free product recovery systems.

7.4 Common Optimization Recommendations

Practical application of free product recovery systems has shown that even under favorable site conditions only a small percentage of the total product released can ever be recovered. Therefore, it is prudent to have established criteria for suspending free product recovery to avoid needless, non-productive operation of the system. As noted in Section 6, a line of evidence approach should be developed to demonstrate that: 1) LNAPL is not migrating and doesn't pose a threat of additional contamination of surface water or groundwater, 2) LNAPL presents no risk to human health or the environment under current and reasonably anticipated future scenarios, and 3) LNAPL recovery has been completed to the maximum extent practicable taking into consideration LNAPL transmissivity data. Following termination of the active recovery, monitoring should be conducted for a specified time period to ensure that product does not re-accumulate in the wells. LNAPL transmissivity testing and recovery estimates should be performed to evaluate the potential for recovery prior to continued system operation. Other treatment technologies may still be required to address potential risk exposure pathways associated with the release once free product recovery is discontinued. These topics are further discussed in the *NAVFAC LNAPL Site Management Handbook* (NAVFAC, 2010) and the *New Developments in LNAPL Site Management* fact sheet (NAVFAC, 2017b).

Reducing the time required to achieve the cleanup objectives can minimize long-term operating costs associated with operating a free product recovery system. Table 7-1 identifies optimization strategies for conventional free product recovery systems. Depending on the type of free product recovery system utilized, recommendations presented earlier for optimizing pump and treat, MPE, and bioventing systems may also be applicable.

Example: *At MCAS New River, free product recovery by a single-pump system in the JP-5 Line Area has been sporadic and diminishing in return. By comparison, trial application of aggressive fluid-vapor recovery (AFVR) has shown promising results at less cost. Therefore, it was recommended that the existing free product recovery system be shut down and the frequency of fluid-level monitoring in the recovery and monitoring wells be increased. An action level for the accumulation of free product in the wells was established and serves as a "trigger" for implementing AFVR.*

Table 7-1. Common Free Product Recovery System Operational Problems and Optimization Strategies

Operational Problem	Potential Causes	Potential Negative Impacts on Performance	Optimization Strategy
The recovery rate declines over time.	• The pump membranes or intake screens are clogged. • Excessive water-level drawdown causes the product to "smear" or adsorb to previously saturated soil. • Biological fouling or mineral buildup of the well screens has occurred.	• The lower recovery rate may extend duration of recovery system operation.	• Clean pump membranes or intake screens. • Adjust the pumping rate to maintain recovery while minimizing drawdown. • Perform well rehabilitation using the appropriate acids and/or biocides.
The design recovery rate has never been achieved.	• Inadequate CSM was used as the basis for design. • Excessive water-level drawdown causes the product to "smear" or adsorb to previously saturated soil. • The wells are poorly developed. • The well screens do not intersect the water table. • The bottoms of the suction tubes are above the water table, causing groundwater mounding, and preventing product flow to the wells.	• The inability to meet design criteria will extend the duration of recovery system operation and allow the free product lens to migrate.	• Adjust the pumping rate to maintain recovery, while minimizing drawdown. • Redevelop poorly developed wells. • Replace wells that are improperly screened. • Measure the depth to water after several days of system shutdown and reposition the bottoms of the suction tubes accordingly. • Further develop the CSM and reevaluate the design elements based on the most current site conditions.
The ratio of fuel recovered to groundwater extracted is low despite the presence of measurable free product.	• The pumps are improperly placed in the recovery wells. • The pumping rate is greater than necessary.	• The treatment and disposal of extraneous water will increase operating costs. • Excessive water-level drawdown will cause product to "smear" or adsorb to previously saturated soil.	• Adjust the pumping rate to maintain recovery, while minimizing drawdown. • Modify skimmer settings to minimize water production. • Adjust the placement of pump in well. • Install additional recovery wells in "hot spots." • Consider implementing an alternate technology, such as MPE.
The free product lens is migrating or the radius of influence is limited.	• The pumping rate is not sufficient. • The system is experiencing prolonged periods of shutdown. • The number of recovery wells is inadequate or they are improperly located.	• Failure to contain the free product will result in incomplete product recovery and increase the duration of system operation.	• Increase the pumping rate in the recovery wells. • Increase the system uptime through a preventative maintenance program. • Install downgradient wells or an interceptor trench to halt product migration.
The LNAPL transmissivity has declined over time.	• All recoverable product at some wells has been removed.	• The continued operation of non-productive wells is not cost effective.	• Shut off non-productive wells or consider modifying them to a bioventing mode.

Table 7-1 (continued). Common Free Product Recovery System Operational Problems and Optimization Strategies

Operational Problem	Potential Causes	Potential Negative Impacts on Performance	Optimization Strategy
			• Measure LNAPL transmissivity and evaluate NSZD as a potential alternative for low risk sites.
The vacuum developed at each recovery well is low.	• Short-circuiting is occurring. • The vacuum pump is not properly sized.	• The inability to establish an adequate vacuum limits the pumping of product and the radius of influence of vacuum gradients and soil venting.	• Operate sections of the well system on a sequential cycle based on the rate of fuel recovery. • Install a properly sized pump.
Product is inadequately separated from the process stream.	• The mixing of fuel, water, and vapor in the process stream is inherent to the extraction technology.	• The incomplete separation of product from the process stream may lead to greater treatment costs, increased maintenance requirements, and potential wastewater discharge violations.	• Review the design and operation of the oil/water separator and other treatment system components.

8.0 NATURAL SOURCE ZONE DEPLETION (NSZD)

8.1 System Description

NSZD is a LNAPL management approach for sites that are deemed low risk because they demonstrate low contaminant mobility and sustained reduction of contaminant mass in the subsurface through volatilization, dissolution, and biodegradation. Similar to MNA, this remedy relies on natural attenuation processes with a program designed to monitor the progress of NSZD toward achieving cleanup objectives. The performance monitoring results are used to calculate the rate at which attenuation is occurring (ITRC, 2018).

As LNAPL becomes more weathered, volatilization and dissolution processes slow. Biodegradation occurs in the saturated and vadose zones, capturing and converting these constituents via oxidation processes to methane and carbon dioxide by utilizing available electron acceptors. Direct biodegradation of LNAPL has also recently been identified as another important depletion mechanism. The key to a successful NSZD remedy is that degradation processes occur at a faster rate than transport processes, effectively immobilizing the source zone. Figure 8-1 illustrates the generalized NSZD process.

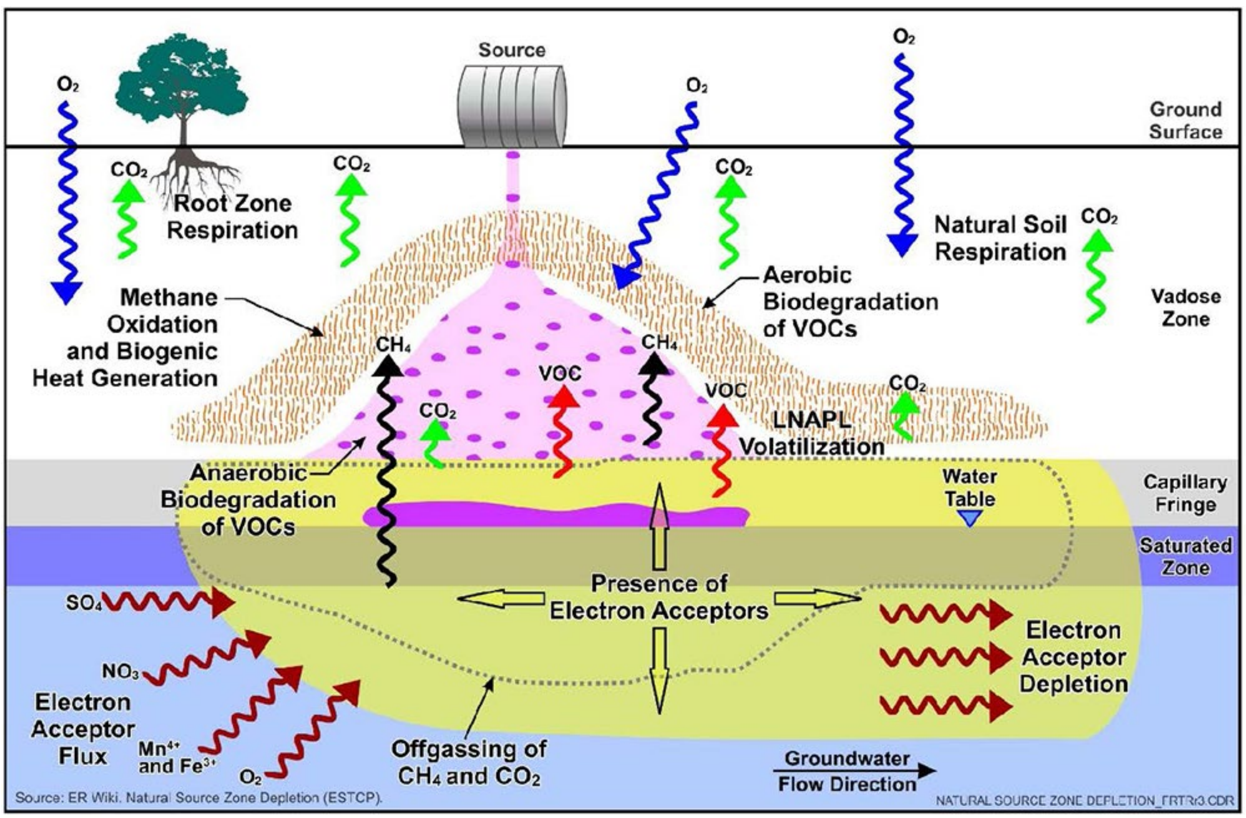


Figure 8-1. Generalized Natural Source Zone Depletion Conceptual Site Model (FRTR, 2020)

8.2 Performance Plots

A key hurdle to implementing NSZD is regulatory and stakeholder acceptance, given that the remedy is passive. By obtaining appropriate site data and using a multiple lines of evidence approach to update the CSM, site managers can demonstrate the following requirements are met and that NSZD is performing successfully (ITRC, 2018):

1) Exposure to LNAPL is controlled (by institutional controls or land use controls).
2) Risk from remaining LNAPL is below acceptable levels.
3) There is insignificant incremental risk reduction benefit to additional active remediation.
4) LNAPL and the associated groundwater contaminant plume are stable (or decreasing) and not migrating.
5) NSZD is effectively remediating residual LNAPL within a reasonable timeframe.
6) Monitoring will continue to confirm long-term effectiveness.

NSZD can be applied at sites where active remediation efforts (e.g., free product recovery) have reached asymptotic conditions in which cost per recovered unit mass of contaminant increases exponentially, and long-term monitoring data trends can be used to demonstrate acceptable risk, asymptotic recovery, and stable source zone and dissolved phase plumes (2, 3, and 4). For example, apparent product thickness and aqueous phase concentration contour maps are often available and can be used to directly measure changes in LNAPL and contaminant plume footprints over time (Figure 8-2). However, it should be noted that the apparent LNAPL thickness in a well relates to the hydrogeologic conditions and characteristics of the LNAPL and soil. The apparent thickness in the well is commonly exaggerated compared to the thickness of the mobile LNAPL interval in the formation and higher resolution tools, such as laser-induced fluorescence (LIF), can provide a better resolution of LNAPL location and in situ distribution (ITRC, 2018).

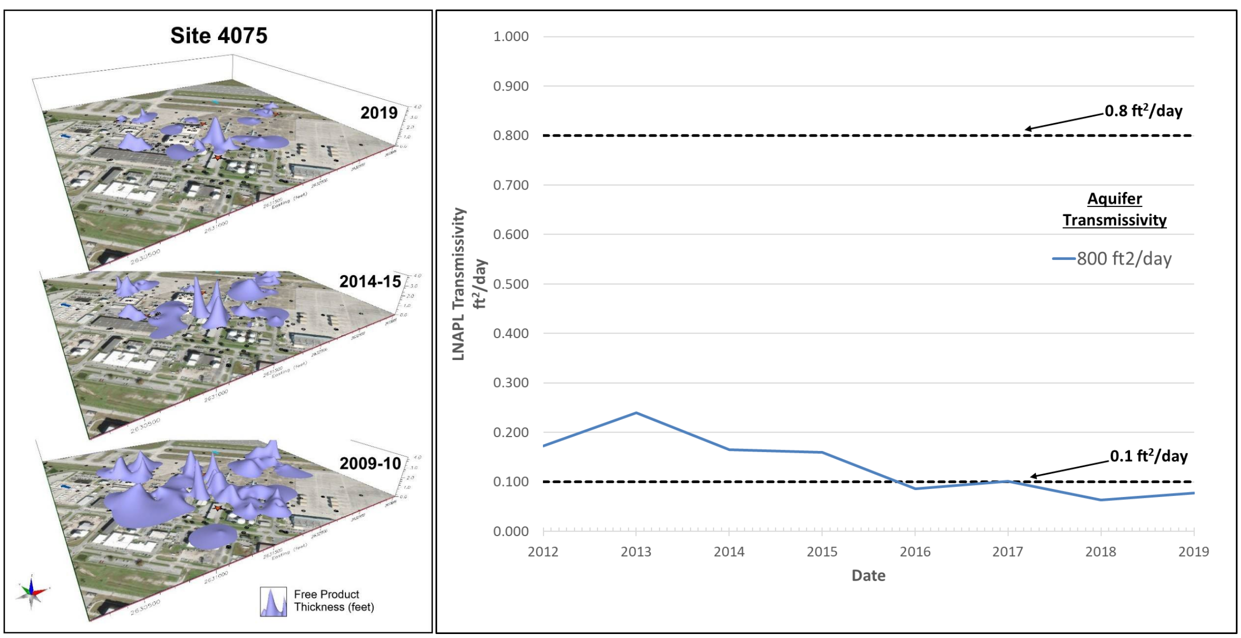


Figure 8-2. Reduction of LNAPL Thickness in Monitoring Wells and Calculated LNAPL Transmissivity at Site 4075, MCAS Cherry Point

Land use control inspections and reporting verify exposure is controlled (1) and NSZD performance monitoring plans and their execution confirm remedy effectiveness (6). Therefore, while some additional data may be collected to verify that LNAPL and the associated groundwater contaminant plume are not migrating (4), most of the supplemental data collection and evaluation is directed towards measurement of NSZD rates (5).

Data collected to verify that LNAPL is not migrating include measurements of LNAPL transmissivity. Several methods exist, including the use of long-term recovery system recovery rate versus drawdown data (Figure 8-2; NAVFAC, 2021a), baildown tests, slug tests, manual skimming tests, and tracer methods (API, 2016; ASTM, 2013).

NSZD biodegradation rates can likewise be estimated by several methods (NAVFAC, 2017b), including:

- The gradient method by which the vertical profile of oxygen consumption is used to calculate flux.
- Carbon traps installed at the ground surface with receptacles for carbon dioxide adsorbent that are sent for laboratory isotopic analysis of carbon-14 to estimate fossil fuel degradation rate.
- Dynamic closed chambers installed at the ground surface with laser-based trace gas analyzers to calculate carbon dioxide fluxes, which are corrected with background flux.
- Thermal monitoring that employs thermocouple strings that measure the heat generated from biodegradation processes in vertical cross-sections, the background-corrected temperatures from which are used to calculate enthalpy changes resulting from LNAPL degradation (Figure 8-3; NAVFAC, 2021a).
- LNAPL compositional changes over time (preferably at least 5 to 10 years in duration) where concentrations of constituents known for preferential biodegradation are compared to control constituents to verify depletion by biodegradation rather than volatilization.

Example: *A remedial system evaluation was performed for Installation Restoration Program (IRP) Site 1 located within the Armitage Field OU at NAWS China Lake. The remedial action objective identified in the ROD is removal of free product to the maximum extent practicable, and the implemented remedy was vacuum-enhanced skimming and free product recovery. Multiple lines of evidence were collected to support a transition from active treatment to NSZD. This included measuring LNAPL transmissivity, updating the CSM with the current extent of LNAPL based on a direct push investigation using LIF direct sensing tools, and determining potential NSZD rates using carbon dioxide flux measurements and subsurface temperature monitoring. NSZD rates were measured using thermal monitoring based on the understanding that heat is generated when the LNAPL degradation product, methane, is oxidized in the vadose zone above the LNAPL source. Temperatures were monitored for a six month period. Figure 8-3 shows the average background-corrected temperature with depth at two monitoring locations. Temperatures were highest at 26 and 36 feet bgs, corresponding to the depths located just above LNAPL, where most methane oxidation is expected to occur. Based on this data, the overall average NSZD rate was determined to be 166 gallons/acre/year (NAVFAC, 2021a).*

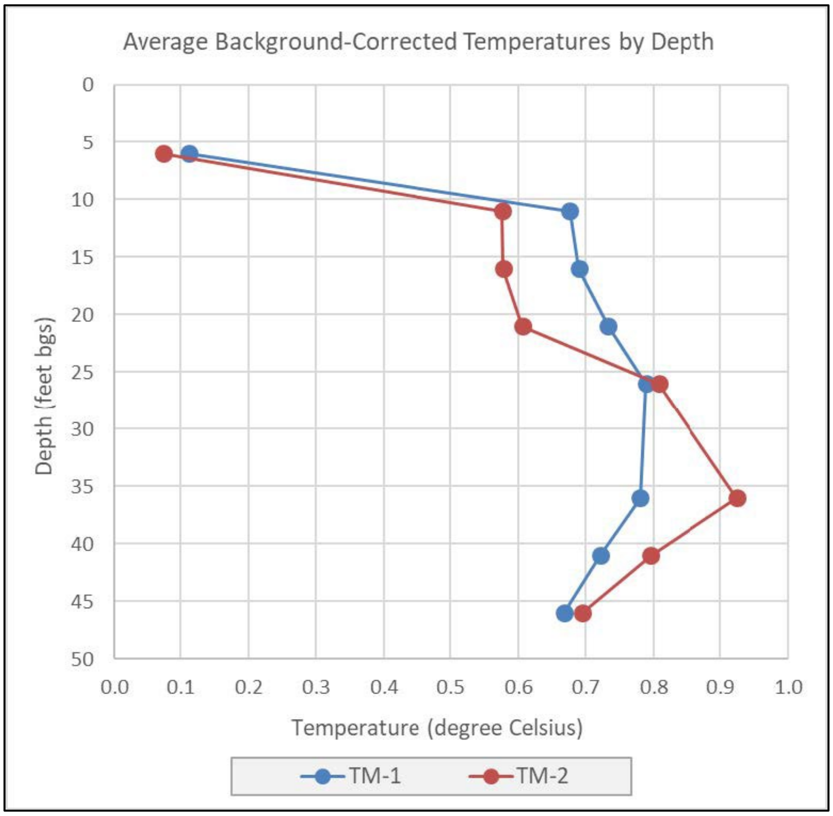


Figure 8-3. Average Background-Correct Temperatures by Depth at Monitoring Wells at Installation Restoration Program Site 1, Naval Air Weapons Station China Lake

8.3 Common Operational Problems

Studies have previously verified that NSZD is appropriate for certain site conditions and performance problems are generally related to sustaining microorganism growth and biodegradation. Table 8-1 outlines problems common to NSZD applications.

8.4 Common Optimization Recommendations

Optimization recommendations for NSZD focus on updating the CSM and ensuring continued achievement of requirements discussed in Section 8.2. Table 8-1 provides guidance on optimizing NSZD. A proposal to implement NSZD must include the following:

- Demonstration that exposure to LNAPL is controlled;
- Risk from remaining LNAPL is below acceptable levels;
- There is insignificant incremental risk reduction benefit to additional active remediation;
- LNAPL and the associated groundwater contaminant plume are stable (or decreasing) and not migrating;

- NSZD is effectively remediating residual LNAPL within a reasonable timeframe; and
- Monitoring confirms long-term effectiveness.

The plan should identify a sufficient number of properly located wells for monitoring the constituents of concerns, biodegradation byproducts, and relevant geochemical parameters. The plan should specify the sampling frequency based on various site-specific factors including proximity to receptors and constituent time-of-travel estimates. Lastly, the proposal must include a contingency plan in the event that performance monitoring indicates that NSZD is not occurring as predicted. The contingency plan should identify the alternative technology selected and clearly specify the criteria under which it is to be implemented.

Table 8-1. Common Operational Problems and Optimization Strategies of Natural Source Zone Depletion

Operational Problem	Potential Causes	Potential Negative Impacts on Performance	Optimization Strategy
The contaminant concentrations have not declined in monitoring wells.	• Source areas or hot spots have not been adequately controlled.	• The presence of a continuing source of contaminants will prevent groundwater cleanup goals from being achieved.	• Evaluate the use of supplemental technologies, such as mobile LNAPL recovery systems or passive skimming.
The LNAPL footprint is expanding or migrating.	• The number of wells is not adequate, or they are improperly located, resulting in inaccurate LNAPL footprint baseline. • New undiscovered release is occurring. • LNAPL mobility estimates were low. • Changing geologic or hydrogeologic conditions, due to earthquakes or long-term changes in water table elevations, may impact LNAPL distribution.	• Failure to maintain containment will allow the footprint to expand in size and potentially reach receptors.	• Install additional wells. • Recollect composition samples for fingerprint analysis to identify LNAPL source. • Remeasure LNAPL transmissivity using an alternative technique. • Consider the use of supplemental or contingency technologies, such as mobile LNAPL recovery systems. • Update CSM for LNAPL distribution using LIF or other high resolution site characterization technique.
The contaminant plume is expanding or migrating.	• The number of wells is not adequate, or they are improperly located, resulting in inaccurate plume baseline. • Dissolution has overcome biodegradation rates.	• Failure to maintain containment will allow the plume to expand in size and potentially reach receptors.	• Install additional wells. • Increase the well pumping rates. • Remeasure NSZD rates using an alternative technique. • Consider the use of supplemental or contingency technologies, such as hydraulic containment systems.
Contaminant degradation is slow or incomplete.	• Electron acceptor distribution to the contaminated zone is not sufficient. • The pH of the groundwater is not between 6 and 8. • Deficiencies of inorganic nutrients such as nitrogen and phosphate may inhibit microorganism growth. • Measured NSZD rates are not sustainable and are observed to decrease over time.	• Microbial activity slows, and cleanup will be incomplete or will take longer than estimated.	• Evaluate the need for nutrient addition and/or pH adjustment. • Evaluate the use of alternate or contingency technologies, such as introduction of electron acceptors.

9.0 PHYTOREMEDIATION

9.1 System Description

Phytoremediation is a treatment technology that uses vegetation and its associated microbiota, soil amendments, and agronomic techniques to provide hydraulic control and/or remove or reduce the toxicity of environmental contaminants. The technology relies upon the natural hydraulic and metabolic processes of plants, and thus is solar driven. Phytoremediation is most commonly applied to shallow soil and groundwater, but is also applicable to sludge, sediments, surface water, stormwater, and wastewater. It is generally used as an in-situ technology but can also be used as an ex-situ technology using hydroponics and/or constructed wetlands (FRTR, 2020).

Phytoremediation can be used to treat a wide range of inorganic (nutrients, heavy metals, and radionuclides) and organic (petroleum hydrocarbons, chlorinated compounds, pesticides, and explosive compounds) contaminants and is applicable to sites where water uptake is desirable for hydraulic/migration control or treatment. Phytoremediation is typically selected when a longer treatment time can be tolerated, and when starting concentrations are relatively low or as part of a treatment train as a polishing step (FRTR, 2020). Full-scale implementation has been documented for phytoremediation for all of these contaminant classes (ITRC, 2009b).

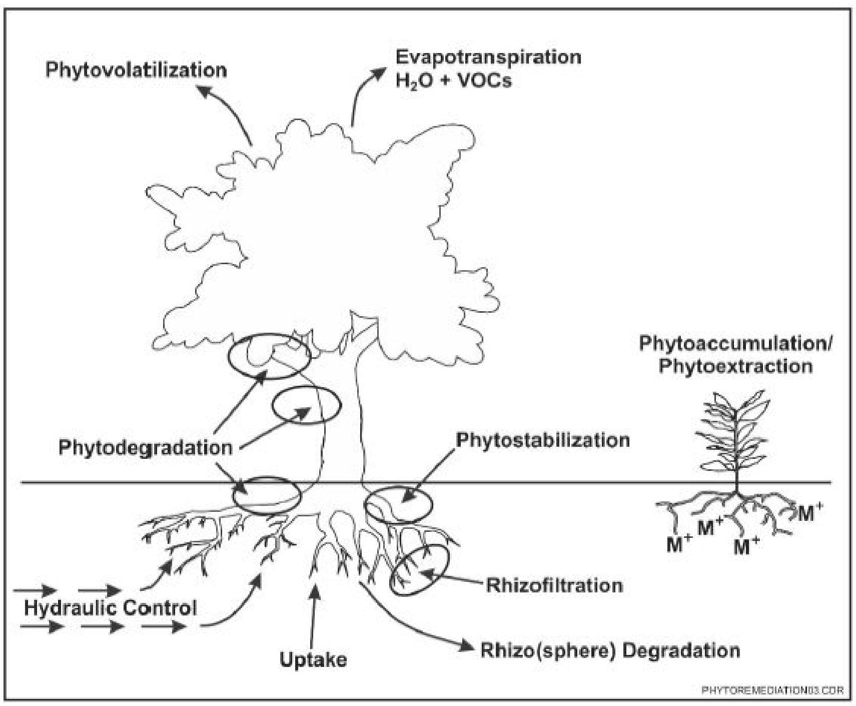


Figure 9-1. Schematic of Typical Phytoremediation Process

Phytoremediation can work through several mechanisms including the following (NAVFAC, 2021b):

Stabilization/Containment Mechanisms

- Phytostabilization – minimizing transport of contaminants by intercepting precipitation and physical stabilization of soil.
- Hydraulic control – use of plants, mainly trees with deep root systems, to consume water (i.e., evapotranspiration) to provide migration control for groundwater.
- Phytosequestration – immobilizing contaminants by chemical precipitation or complex formation with root exudates in the rhizosphere, as well as near the soil surface with interactions between natural organic material derived from plant decomposition.

Removal/Degradation Mechanisms

- Phytoextraction – uptake of contaminants into plant tissue, usually accompanied by periodic harvesting and disposal of plant material.
- Phytovolatilization – movement of contaminants from soil or water through the plant and transpired to the atmosphere.
- Degradation – transformation of contaminants in the root zone (rhizodegradation) or stems/leaves (phytodegradation).

References for example case studies of these various phytoremediation mechanisms are provided in the NAVFAC Fact Sheet, Phytoremediation Advances (NAVFAC, 2021b).

9.2 Performance Plots

The performance of phytoremediation systems for treatment of shallow groundwater can be illustrated by plotting groundwater elevations (i.e., for hydraulic control) or contaminants of concern from groundwater monitoring wells in the treatment area versus time. Contaminant of concern trends in the shallow groundwater can also be assessed spatially using isoconcentration contour maps at various time intervals with remedial goal contours and groundwater flow direction included. Changes in contaminant mass over time in the treatment zone can also be estimated using a 3-D interpolation of the groundwater concentration data. The typical performance plot and isoconcentration contour map is characterized by decreasing contaminant of concern levels and a retardation of the contaminant of concern plume growth over time, respectively. A plot of select contaminant of concern levels in groundwater versus time with remedial goal levels is shown in Figure 9-2. Isoconcentration contaminant of concern contour maps at two time points, at the start of phytoremediation and after 15 years of monitoring, is presented in Figure 9-3.

Example: *Two phytoremediation plantations of hybrid poplar trees, referred to as the "north" and "south" plantations, were planted at Naval Base Kitsap, Keyport, Washington in 1999 to work in concert with MNA to remove and treat VOC-contaminated groundwater and reduce the long-term potential for VOC migration from the site. Figure 9-2 shows a decreasing trend in contaminant of concern concentrations including TCE, cis-1,2-DCE, and VC from MW1-16 located in the South Planation from baseline levels before planting to below remedial goal levels over the course of 15 years of monitoring. Figure 9-3 shows an upper aquifer groundwater TCE* *concentration contour map at the South Plantation at the start of phytoremediation in 1999 (left) and the contracted TCE plume in 2014 (right) (NAVFAC, 2015a).*

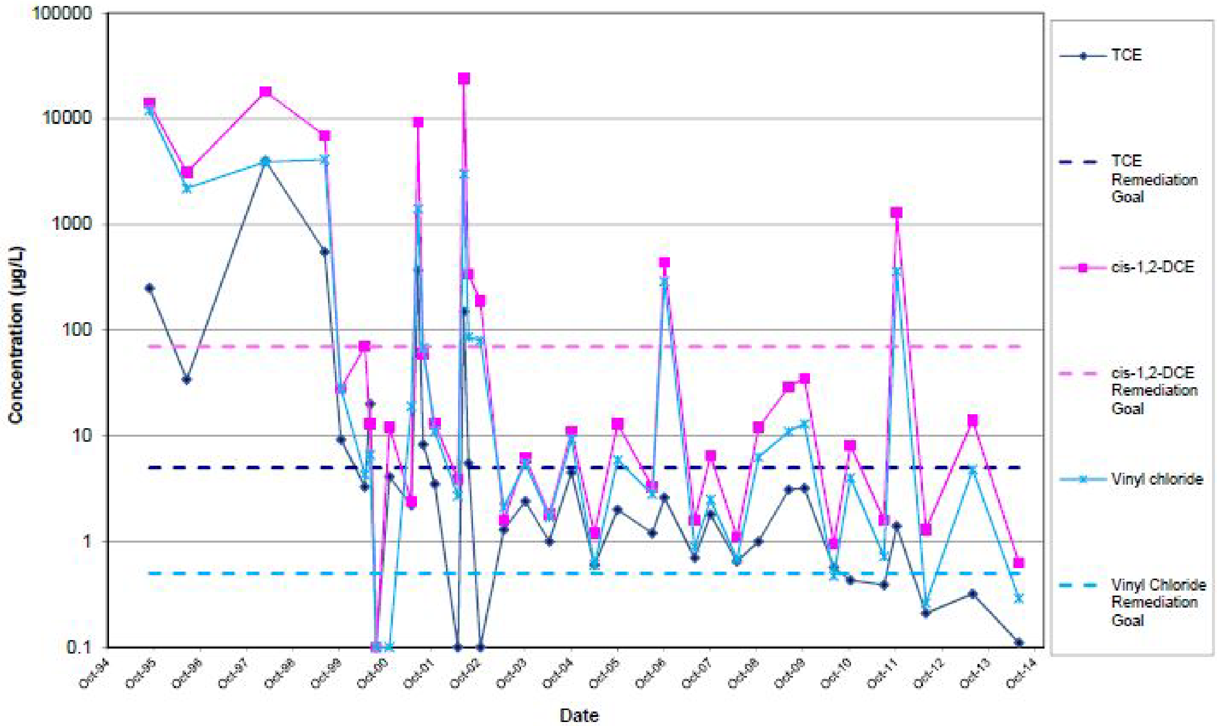
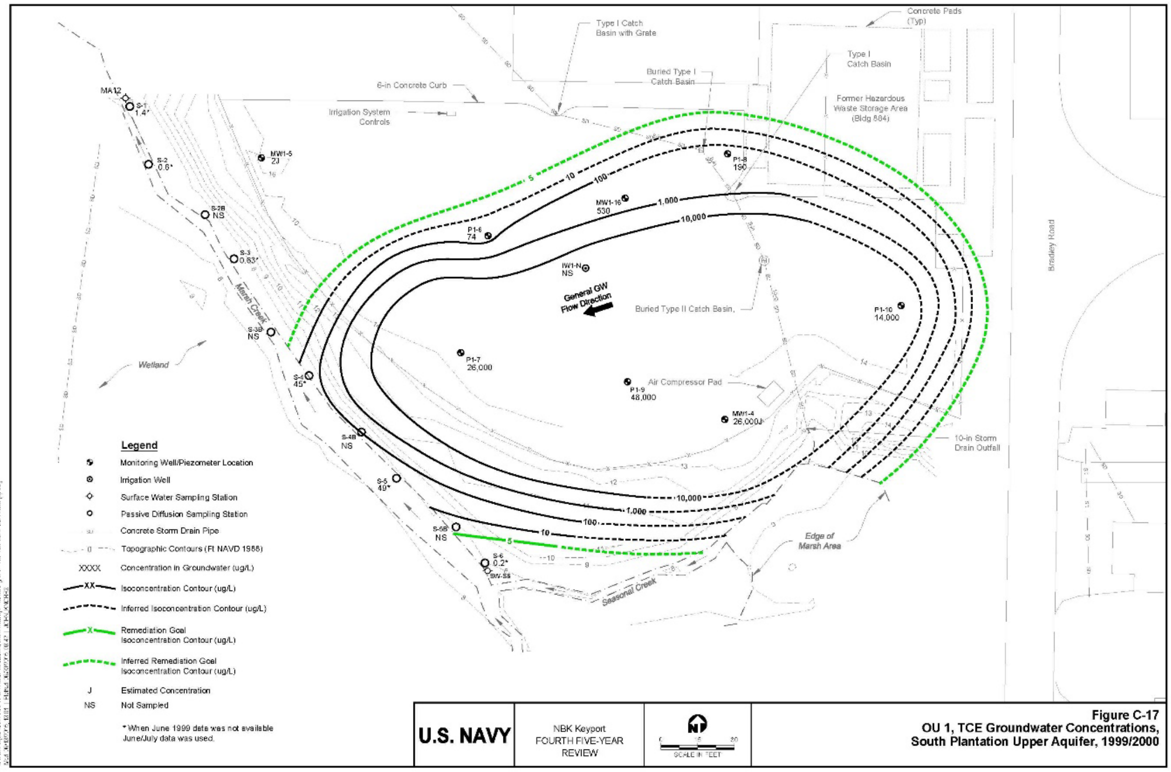


Figure 9-2. Plot of Phytoremediation System Performance



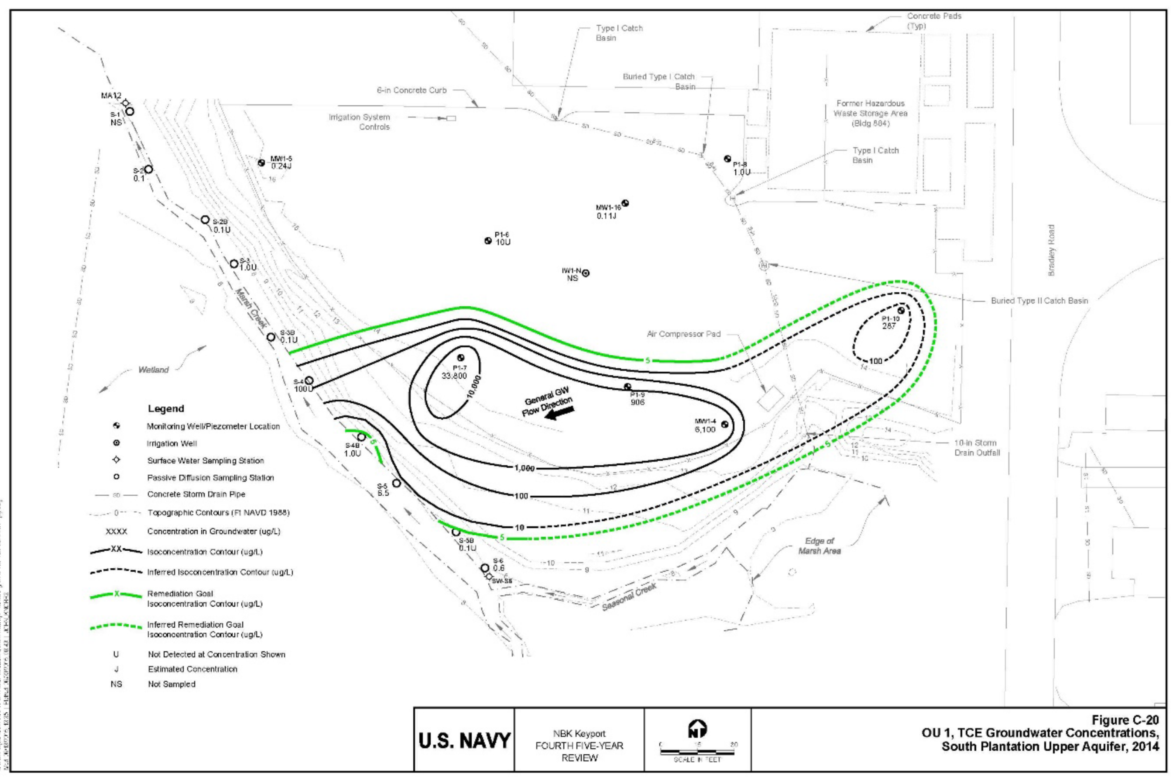


Figure 9-3. Contour Maps of Phytoremediation System Performance

9.3 Common Operational Problems

The main factors that cause operation problems for phytoremediation systems are the lack of plant care and site upkeep, which inhibits the development of deep root systems and a healthy canopy and can influence remedial performance (ITRC, 2009b).

Common operation problems include but are not limited to the following (ITRC, 2009b):

- Lack of monitoring the plant growth conditions, including canopy and root growth, and climate conditions. Newly-planted areas generally require more frequent monitoring and care compared to established plants.
- Improper irrigation of the phytoremediation system. Irrigation systems may need to be installed or modified to ensure a vigorous start to the phytotechnology system. Excessive irrigation can mobilize contamination from soil to ground- or surface water.
- Climate change-induced periods of drought or increased flooding events can have detrimental effects on plant growth and effectiveness of phytoremediation.
- Improper selection of plant species given site-specific factors (e.g., soils, weather extremes). This may include unknown or inappropriate soil types for the selected species, or a decrease in habitat value where non-native species are used.
- Excess nitrogen fertilizers have been shown to impact receiving water bodies located downgradient and can have a detrimental effect if not managed carefully. Most chemical fertilizers should not be applied immediately before a heavy rain event and/or before storm water management systems have been installed.
- Weeds should be controlled to reduce competition with the selected phytotechnology plants and prevent the spread of nuisance plants. When using herbicides, care should be taken to select an herbicide that is not detrimental to the desired plant, and the application time and methods should minimize spray drift.
- All plant communities should be monitored for signs of stress or damage from plant disease or insects. Larger pests such as mice, rats, rabbits, moles, gophers, groundhogs, beavers, deer, migratory birds, and other species may also be attracted to phytotechnology systems and can pose significant risks to the success of the phytotechnology system by damaging or consuming the vegetation.
- Special care should be given when operating mowing equipment so as to not damage or destroy the desired species, such as damaging the bark when using rotary trimmers to cut weeds around trees. A weed control program should be implemented to minimize the growth of undesired and competitive species.

Diseases in a tree stand generally develop when some form of stress or damage to the vegetation creates weaknesses where the disease can take effect. These conditions or events include water damage from floods, chemical damage from road salt, and physical damage such as nicks or scrapes during mowing or other weed control activities or from wind, animals, or other infestations. In some cases, the contaminants that are to be addressed with the phytotechnology system may cause the stress leading to a disease infestation. If this is the case and complete devastation results, the site will likely need to be replanted periodically (ITRC, 2009b).

The plant material generated from mowing activities or natural litter may need to be collected and treated as if it is a hazardous waste until appropriate testing for contaminant accumulation can be conducted. If contaminant concentrations in plant tissues do exceed regulatory limits, the cut plant material or litter will need to be treated as a hazardous waste. To prevent the migration of plant litter prior to collection, fencing and netting may need to be considered (ITRC, 2009b). Table 9-1 lists these and other problems applicable to phytoremediation.

9.4 Common Optimization Strategies

Optimum operation of phytoremediation systems usually includes establishing and maintaining vigorous plant growth, development, and health by providing an optimum growth environment, maintaining optimum soil nutrient content and water supply, reducing competition and predation, and performing seasonal activities that prepare the plantation for the next season (ITRC, 2009b). Technical experts experienced with plant establishment and growth in the specific remediation project region should be consulted during project planning and implementation, including those with plant nursery or native plant knowledge.

Soil preparation for a phytotechnology plantation is similar to that undertaken in agriculture, including tilling, fertilizing, planting, and irrigating, and should be done according to application guidelines and rules. Compact soils can restrict root penetration and need to be dealt with using tilling or harrowing. Either during or after the soil is tilled, soil amendments and an initial fertilizer application can be added into the matrix (ITRC, 2009b).

Typically, regular fertilizations can be done in early spring to help the new growth and in late fall to prepare the vegetation for winterization. When dealing with sites impacted with biodegradable organic contaminants, the inorganic nutrient demand from the microbes also needs to be considered along with the demand from vegetation (ITRC, 2009b).

A general rule of thumb is that during establishment and throughout the growth of the vegetation, plants should receive a total of 1 to 2 inches of water per week, or an amount recommended for the plant species utilized, including both precipitation and supplemental irrigation. An irrigation system can provide a backup in case of severe drought. Furthermore, applications of a liquid fertilizer may best be applied using the irrigation system (ITRC, 2009b). Phytoremediation should be carried out by experienced practitioners familiar with plant establishment and growth in the specific region. Those with plant nursery knowledge, or native plant knowledge, should be on the project team.

Weed control may be necessary throughout the life of the project but is more important for the first few years before the desired canopy has fully formed and can shade any undesired growth from out-competing. Weed control can be accomplished by mechanical methods such as mowing, smothering, mulching, or manual removal or through the use of herbicides (ITRC, 2009b).

Monitoring the site for diseases should also be part of standard operations and maintenance activities. Depending on the disease, different control and preventative measures can be employed, such as additional fertilizer, other biological agents that attack the disease rather than the host, or sprays containing plant antibiotics (ITRC, 2009b). Phytoremediation designs should also consider selecting a mixed culture, including both native plants and other phytoremediation species that can increase the overall ecosystem health and help to avoid having entire phytoremediation systems decimated by a disease.

Mowing groundcovers and pruning/thinning tree stands may also be needed to maintain a healthy stand, control weeds, strengthen plant structure, promote denser canopy, and minimize damage from storms. Cutting down dead or dried grasses or plants should be done annually or as needed. Cutting in the spring should be done prior to the emergence of new leaf growth or before new seeds or annual plants are replanted at the site. Branches on trees and woody shrubs can be pruned during the late winter, spring, or summer months (ITRC, 2009b).

For controlling infiltration, soil mounding, contouring/grading, and impermeable or semipermeable barriers can restrict or control total infiltration. Common barrier materials include compacted clay, low- and high-density polyethylene liners and landscape tarp (polypropylene mesh). To minimize runoff, higher-permeability materials such as sand, gravel, or cobble placed in layers or along boundaries can be used to capture, store, and/or convey the storm water as desired based on management requirements (ITRC, 2009b).

Entry into the site may need to be restricted either to minimize potential exposures to human and ecological receptors. Fencing provides a minimum level of protection for these needs but can also serve other purposes in addition to providing security for the site (ITRC, 2009b).

Typically, the plant litter drop occurs at specific times throughout the growing season, and collection, if required, should be scheduled accordingly. To prevent the migration of plant litter prior to collection, fencing and netting may need to be considered. Furthermore, plant litter buildup may need to be removed simply to maintain storm water control systems (ITRC, 2009b). Table 9-1 provides other guidance on optimizing phytoremediation system performance.

Treatment wetlands, or constructed treatment wetlands, are a type of phytoremediation where saturated, hydric soils or other saturated substrates are used in conjunction with plants suited for growth in continuously saturated conditions. Treatment wetlands are typically used to treat water, such as stormwater runoff, and have specific considerations which are not detailed here due to the breadth of the topic. However, one of the major considerations dictating the success of a well-designed treatment wetland is that of hydraulics ─ ensuring that no part of the treatment wetland is either too dry or overflows, and that flows into and out of the wetland allow for suitable retention times for contaminant treatment. There are many resources available on treatment wetland design, and practitioners should consult these technical resources.

Table 9-1. Common Phytoremediation System Operational Problems and Optimization Strategies

Operational Problem	Potential Causes	Potential Negative Impacts on Performance	Optimization Strategy
Lack of monitoring the phytoremediation system parameters including plant growth conditions, and climate conditions.	• Infrequent monitoring of local weather station data or not setting up an on-site meteorological station. • Infrequent measurements of plant height, trunk growth or diameter, and leaf area index.	• The growth, development, and health of the vegetation directly influence the ability of the system to perform the desired remediation and may increase the length of the treatment period.	• Monitor climate conditions (including temperature, barometric pressure, relative humidity, precipitation, wind speed and direction, and solar radiation. • Record physical measurements of the canopy and root (using a hollow-core drill) development.
Prolonged periods of drought, increased flooding events, or improper irrigation and fertilization.	• To maintain vigorous plant growth the water supply needs to be at optimum conditions. • Soil agronomic samples need to be collected and guidance on soil amendments needs to be consulted to optimize plant nutrition. • Prolonged period of drought may result in a depressed water table.	• Excessive irrigation or flooding events can mobilize contamination from soil to ground- or surface water. • Hydraulic control or phytoextraction of dissolved phase contaminants become ineffective if plant roots do not intercept groundwater when water table is depressed. • Excess nitrogen fertilizers have been shown to impact receiving water bodies located downgradient and can have a detrimental effect if not managed carefully. • Nutrient deficiencies can result in wilting, yellowing, and leaf curling.	• Generally, plants should receive a total of 1–2 inches of water per week, or an amount recommended for the plant species utilized and region, including both precipitation and supplemental irrigation. • Irrigation with contaminated water from the site may be preferred to clean water because it will allow the plant to adapt to the contaminant concentrations in the groundwater. This approach may also address negative impacts during periods of prolonged drought conditions. • Species-specific water demands may need to be calculated using measurements of transpiration. These can be measured using sap flow sensors. • The water-holding capacity of the soil should also be considered and can be measured using soil moisture probes inserted into the root zone. • Typically, regular fertilizations can be done in early spring to help the new growth and in late fall to prepare the vegetation for winterization.

Table 9-1 (continued). Common Phytoremediation System Operational Problems and Optimization Strategies

Operational Problem	Potential Causes	Potential Negative Impacts on Performance	Optimization Strategy
Monitoring data reveals contaminant concentrations that are higher than expected compared to the design basis for phytoremediation.	• Insufficient CSM developed prior to phytoremediation design. • Unknown contaminant source area remains at site.	• Phytoremediation cannot effectively treat contaminant concentrations at the site. • Remedial goals cannot be achieved	• Perform additional site investigation to update the CSM. • Evaluate alternative remedial technologies for source area treatment, in addition to or in place of phytoremediation.
Improper weed and pest control.	• Weed and pest control may be necessary throughout the life of the project and not just for the first few years of operation.	• Hand removal of weeds is preferred. • The herbicide selected at the site may be detrimental to the desired plant. • Poor weed control could increase competition with the selected phytotechnology plants and augment the spread of nuisance plants. • Pests can pose significant risks to the phytotechnology system by damaging or consuming the vegetation.	• Weed control can be accomplished by mechanical methods such as mowing, smothering, mulching, or manual removal or through the use of herbicides. • Fencing can be installed around the site, or individual plants to prevent pests from damaging plants. • Burrowing animals can be controlled by installing a trench around the perimeter of the site and filled with cobble that cannot be burrowed through.
Damage to plants during mowing or trimming of plants.	• Operation of rotary trimmers to cut weeds around trees can damage the bark of the desired plant species.	• Diseases in a tree stand generally develop due to physical damage such as nicks or scrapes during mowing or other weed control activities.	• Plants may need to be protected through installation of wire baskets, trunk guards, guidelines, ties, and stakes. • Planting multiple types of plant species is a good practice to mitigate against the potential for diseases that are specific to one particular species.
Disposal of potentially contaminated plant waste.	• Phytoextraction using some plant species may uptake high levels of metals or into the above ground tissues.	• Cut plant matter may be hazardous waste and cannot be left on the ground. It may need to be collected and disposed as a hazardous waste.	• To prevent the migration of plant litter prior to collection, fencing and netting may need to be considered. • In some cases, the plant material may be harvested and sold as a cash crop to offset some of the remedial costs.

10.0 PERMEABLE REACTIVE BARRIERS

10.1 System Description

Many types of PRBs are used to passively treat groundwater in situ (FRTR, 2020). PRBs provide a semi-permanent, in-situ, low maintenance method for treating contaminants dissolved in groundwater. A PRB is installed in the flow path of the contaminated groundwater, allowing the contaminants to be treated as the plume migrates through the reactive media. The reactive agents in the PRB vary depending upon the contaminants of concern and the desired remediation mechanism. PRBs have been designed to facilitate biological degradation, chemical oxidation/reduction, metals precipitation, removal via sorption, and air sparging. They can treat a large variety of groundwater contaminants, including organics, metals (e.g., chromate), ions (e.g., ammonium), energetic compounds, perchlorate, and radionuclides.

Contamination limited to the upper portion of a surficial aquifer may be addressed with a "hanging" PRB, while deeper contamination may require that the PRB extend to a lower confining layer to prevent underflow. A schematic drawing of a PRB extending to a lower confining layer is shown in Figure 10-1.

There are a number of ways to reduce the capital costs associated with the construction of a PRB. One of these ways is by alternating low-cost, impermeable barriers with reactive barriers, forming a "funnel and gate" system. This method ensures that all contaminated groundwater flows through a reactive barrier, without requiring the installation of a continuous reactive wall. A second way to reduce capital costs is to identify lower-cost construction techniques, such as a one-pass trencher or injection of reactive media using direct-push drill rigs. Another option is to use alternative, lower-cost reactive media, including vegetable oil or biowall mulch.

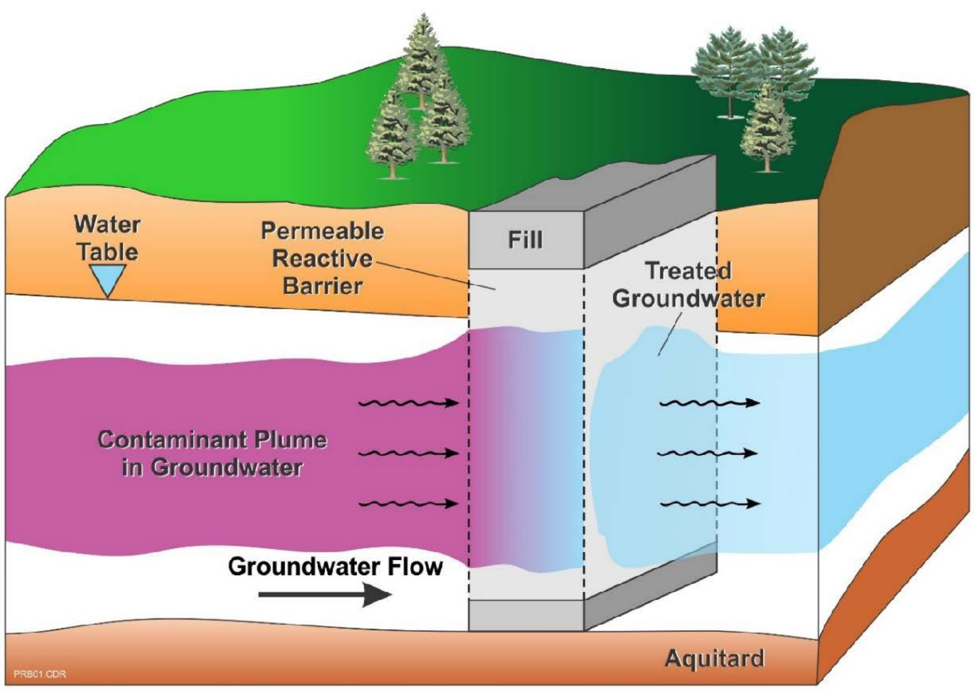


Figure 10-1. Permeable Reactive Barrier

The passive, in-situ nature of the PRB system yields a system with low operating and maintenance costs. When designed correctly, the requirements for energy input, equipment repair, and manpower are very low when compared to other active remedial systems, such as pump and treat.

10.2 Performance Plots

Figure 10-2 depicts a conceptual contaminant concentration profile along the flow path through a PRB. The plot can be prepared using results from performance monitoring wells located within and around the PRB. As contaminants enter the reactive barrier, they are treated via the particular remediation mechanism for that contaminant and media. For most PRBs, the reactive capacity of the wall will be depleted over time.

Once the PRB is not able to reduce contaminant concentrations to the required cleanup level, it will need to be rejuvenated or replaced. Preferential flow paths may develop within the PRB resulting in different flow velocities within different parts of the barrier. Consequently, the residence time of the contaminants within the PRB may represent a range, rather than a given value, and a factor of safety should be included in the design.

It is important to monitor the hydraulic performance of PRBs to ensure that groundwater contaminants are intercepted by the reactive media and do not bypass the PRB. Potentiometric surface maps should also be prepared from water levels measured in the monitoring wells. The maps should be evaluated for groundwater mounding upgradient of the PRB and for other hydraulic evidence of changes in groundwater flow that could potentially transport contaminants around or beneath the PRB.

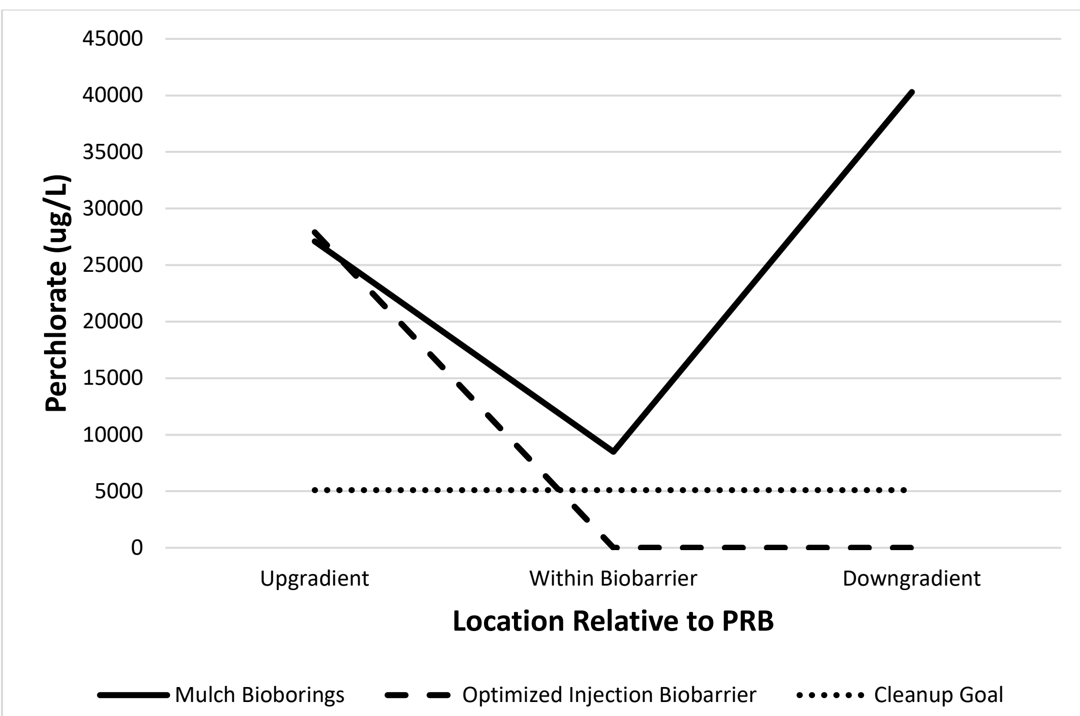


Figure 10-2. Performance Plot of Permeable Reactive Barrier Pilot Study at Former Naval Weapons Industrial Reserve Plant McGregor

Example: *A biobarrier pilot study was performed at Former Naval Weapons Industrial Reserve Plant McGregor, Texas, to treat perchlorate in groundwater. The biobarrier consisted of a series of 12-inch diameter bioborings backfilled with a treatment zone material consisting of 60% crushed limestone drainage aggregate, 20% mushroom compost, and 20% commercial emulsified vegetable oil-saturated wood shavings. Samples were collected from monitoring wells located upgradient of the biobarrier, within the biobarrier treatment zone, and downgradient of the biobarrier. These data suggested that the mulch-compost bioborings did not have a large enough radius of influence to create a continuous reactive zone; therefore, it was not providing sufficient treatment of perchlorate as groundwater passed through the permeable treatment zone. As a next step in the pilot study, emulsified vegetable oil was injected directly into the bioborings to enhance the reactive treatment zone. Significant decreases in perchlorate concentrations were observed following the injections. Based on these pilot study results, the full-scale design has been optimized to use a series of injection points and injection of emulsified vegetable oil to form the reactive zone of the biobarrier without drilling and backfilling oversized bioborings.*

10.3 Common Operational Problems

Thorough site characterization combined with careful design and construction techniques can minimize the potential of developing operational problems. This includes having a well-developed hydrogeologic CSM as the basis for the PRB design to ensure that the contaminant plume is intersected and groundwater flows through the reactive zone of the PRB. Resolving problems that may develop can require significant effort and resources. Table 10-1 lists potential problems applicable to PRBs.

10.4 Common Optimization Recommendations

Because the PRB is a passive system, most of the system optimization must occur during system design and construction. Designs typically include redundancy (e.g., thicker treatment wall; multiple walls) and imbedded infrastructure to allow rejuvenation for increased longevity and effectiveness. A groundwater monitoring network must be installed to track the performance of the PRB and to identify breakthrough or bypassing of the system. Consequently, the greatest opportunity to minimize operating costs usually exists in optimizing the monitoring program. Table 10-1 identifies several optimization strategies for PRBs.

Table 10-1. Common Permeable Reactive Barrier Operational Problems and Optimization Strategies

Operational Problem	Potential Causes	Potential Negative Impacts on Performance	Optimization Strategy
The system performance cannot be accurately evaluated.	• The performance-monitoring program is not adequate.	• An inadequate performance-monitoring program may fail to detect other potential problems identified in this table.	• Multi-depth monitoring wells should be placed: upgradient and downgradient of the reactive barrier to confirm treatment; laterally to detect bypassing; and, within the reactive barrier to warn against breakthrough.
The contaminated groundwater bypasses the PRB.	• The reactive barrier and/or funnel system are not wide or deep enough to capture all of the contaminated groundwater. • Bypass occurs at the junction between funnel and reactive barrier. • Design or construction limitations (e.g., smearing or compaction of low-permeability material along wall/soil interface) create an effective barrier with lower permeability than the surrounding lithology, causing contaminated groundwater to flow under or around the PRB.	• Untreated contaminants will migrate downgradient, allowing the plume to enlarge and potentially reach receptors. The larger area of contamination will also result in increased remediation time and require expanding the remediation system.	• Extend the reactive or impermeable barrier to intercept the path of the contaminated groundwater • Use grout injection to seal post-installation leaks between the barrier and the funnel walls or the underlying confining layer. • Remove low-permeability material from smear zone through targeted augering.
The contaminated groundwater breaks through the PRB.	• Short-circuiting due to preferential flow paths is occurring. • Mineral precipitation or passivation occurs in the reactive cell and reduces availability to the active media. • Inadequate residence time in the PRB prevents adequate treatment of contaminants.	• Partially treated contaminants will migrate downgradient, allowing the plume to enlarge and potentially reach receptors. The larger area of contamination will result in increased remediation time and require expanding the remediation system.	• Rejuvenate or re-install the PRB. • Evaluate the use of an alternate technology if precipitation or passivation cannot be prevented. • Install additional rows of injections wells (e.g., biobarrier) to allow for additional substrate injection and more residence time.
The contaminated groundwater breaks through the funnel system.	• The permeability of the funnel is greater than the design permeability. • The impermeable barrier is not continuous.	• Contaminated groundwater will flow downgradient, allowing the plume to enlarge and potentially reach receptors. The larger area of contamination will result in increased remediation time and require expanding the remediation system.	• Upgrade or re-install the impermeable barrier.
Permeability of the PRB decreases over time.	• Mineral precipitation or sediment accumulation occurs in the reactive cell and reduces or prevents the flow of contaminated groundwater through the reactive cell.	• The decreased permeability will result in groundwater mounding and bypassing the PRB. • Contaminated groundwater will flow downgradient, allowing the plume to enlarge and potentially reach receptors. The larger area of contamination will result in increased remediation time and require expanding the remediation system.	• Rejuvenate or re-install the PRB. • Evaluate the use of an alternate technology if precipitation or sediment accumulation cannot be prevented.

11.0 IN-SITU ACTIVATED CARBON

11.1 System Description

Activated carbon (AC)-based amendments are being applied for the in-situ remediation of a wide range of organic contaminants in groundwater (NAVFAC, 2019a). AC consists of an aqueous suspension of various forms of small-sized carbon particles or as a colloid (USEPA, 2018), which can flow into aquifer flux zones.

AC is injected under pressure using well points or added to the subsurface in an open excavation prior to backfilling. Injection pressures are generally kept below the level needed to fracture the unconsolidated subsurface soils, but in some cases the design may include fracturing to increase the mass and distribution of AC.

After delivery to the subsurface, AC particles attach strongly to the aquifer matrix, where they can act as passive adsorbents for contaminants of concern (Figure 11-1). By adsorption, AC immobilizes the contaminants of concern to prevent further horizontal and vertical migration in groundwater within the treatment area. This can help mitigate long-term mass flux to downgradient receptors or facilitate natural attenuation within the distal portions of the plume. Adsorption onto the AC matrix is enhanced by its highly porous internal structure ranging in size from the largest macropores (>50 nanometer [nm]) down to the smallest micropores (<2 nm). The micropores tend to serve as adsorption sites for contaminants such as TCE and benzene due to their similar dimensions. Different AC products will have varying adsorption capacities based on several factors. The saturation adsorption capacity of a given AC media is based on the contaminant properties, site-specific environmental factors, as well as being a function of the media's microporosity and surface acidity.

Potential AC applications may include treatment of source areas and/or downgradient portions of the plume, as well as to provide a permeable reactive barrier to prevent contaminant migration to protect sensitive receptors and to mitigate further plume expansion. In-situ AC has also been applied at full scale to treat PFAS; however, additional research is needed to evaluate the long-term efficacy of the emplaced amendments. Factors such as adsorption capacity, matrix interferences, amendment longevity, and potential for PFAS back diffusion require future study.

AC also has been combined with other amendments such as zero valent iron (ZVI), calcium peroxide, nutrients, and bacteria strains to facilitate secondary reactions to eliminate contaminants of concern. These amendments are either directly incorporated into the AC amendment mixture or delivered separately in a treatment train approach. Applying these additional treatment amendments may serve to regenerate the AC surface area and create a dynamic equilibrium between contaminant influx, adsorption, and degradation to allow for continued adsorption of contaminant mass flux in groundwater (FRTR, 2020). More research is needed to fully understand the portion of contaminant reduction due to adsorption versus degradation.

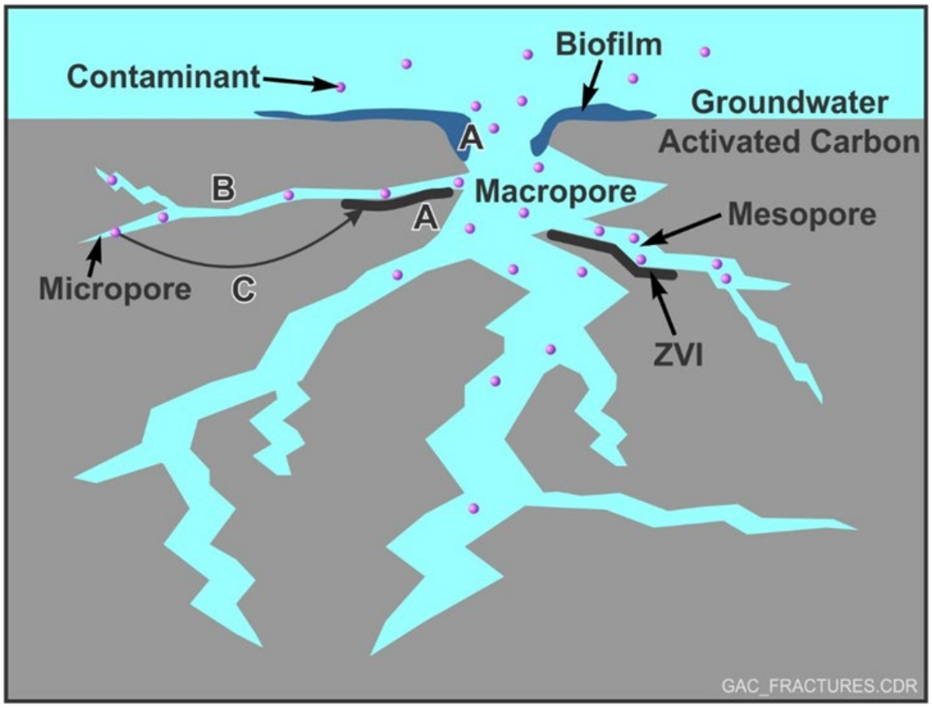


Figure 11-1 Conceptual Diagram of AC-Based Contaminant Removal Process (FRTR, 2020). Illustrates the following processes: (A) direct adsorption and/or degradation by reactive amendment, (B) micropore adsorption, and (C) desorption/diffusion form micropore followed by degradation via reactive amendment (Modified from Fan et al., 2017)

11.2 Performance Plots

The effectiveness of in-situ AC may be determined though performance plots. The data that should be collected for an in-situ AC treatment event are described below.

- Pre-injection sampling. Contaminant concentrations prior to AC injection will provide the baseline for source reduction. The site-specific amendment loading can be calculated based on laboratory measurements of the adsorption capacity of the AC based on contaminant concentrations and the presence of any competing species (e.g., organic carbon).
- Injection measurements. The volume and location of AC injected will provide information on the system design. Groundwater quality measurements (e.g., pH, alkalinity, oxidation-reduction potential, and conductivity) will provide an understanding of changing site conditions. Contaminant concentrations during injection will allow an assessment of system design and treatment effectiveness.
- Post-injection soil borings. Soil cores recovered from boreholes are often used to visually evaluate the distribution of AC in the subsurface. AC is black making it easy to observe.

- Post-injection sampling. Contaminant concentrations after treatment will determine the reduction of the source area and identify any rebound effects. An example plot of contaminant concentrations over time is shown in Figure 11-2.

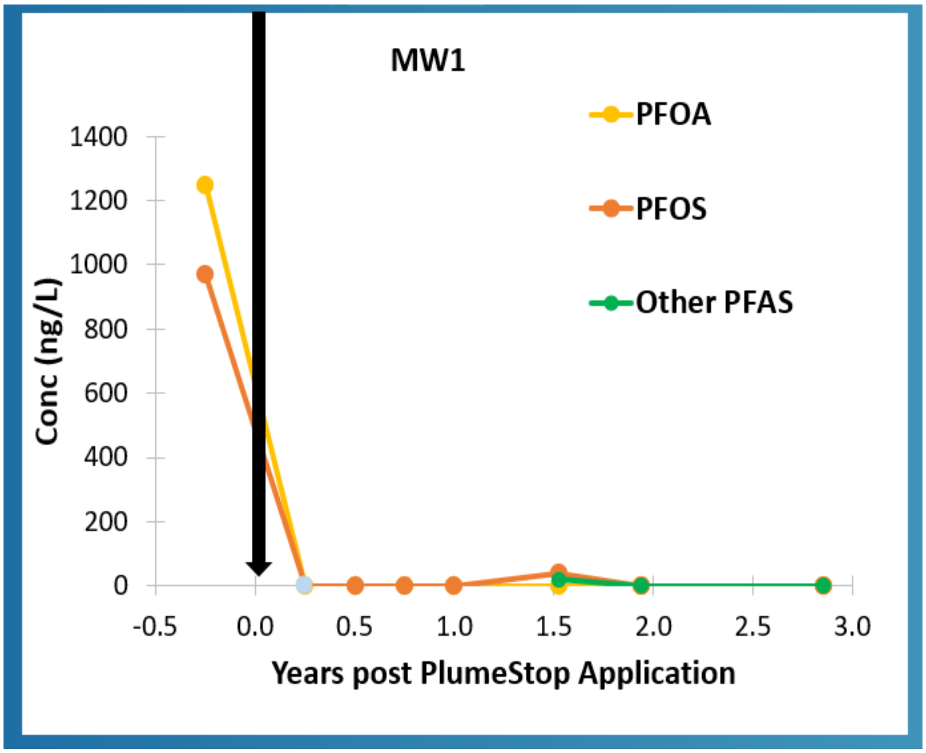


Figure 11-2. PFAS Results After an Injection of Colloidal Activated Carbon (Reproduced with Permission from Regenesis Bioremediation Products)

11.3 Common Operational Problems

In-situ AC treatments must be conducted under carefully controlled conditions. The existing site conditions must be evaluated to determine the appropriate execution and use of this process. The effectiveness of in-situ AC is dependent on site conditions, treatment design, and the consideration of post-AC treatment effects. The two most critical success factors for AC treatment projects are the effective distribution of the AC and amendments if applied in the treatment zone and the ability of the AC adsorption and amendment to meet the remediation goal of the contamination. Common operational problems related to in-situ AC treatment are provided in Table 11-1.

11.4 Common Optimization Recommendations

Optimization strategies typically cannot be applied during an AC injection treatment event; instead, optimization strategies focus primarily on correcting operational problems for subsequent treatment events. Data collected during the AC injection and subsequent performance monitoring data should be evaluated as part of the optimization process. Optimization problems resulting from most site condition limitations will require the use of an alternative technology. Other optimization recommendations include design modifications and the combined use of technologies. These optimization recommendations provide a general approach as appropriate design modifications must be determined on a site-specific basis. Optimization strategies for design of the injection process are discussed in Section 16. Common optimization strategies for in-situ AC are provided in Table 11-1.

Table 11-1. Common Operational Problems and Optimization Strategies for In-Situ AC Treatment

Operational Problem	Potential Causes	Potential Negative Impacts on Performance	Optimization Strategy
The contaminant concentration has not declined in the monitoring wells.	• Too much contamination is present for effective treatment. • Source areas or hot spots have not been adequately controlled or identified. • The injection wells are improperly located. • Preferential pathways prevent adequate distribution of AC and amendments.	• The presence of a continuing source of contaminants will prevent cleanup goals from being achieved.	• Perform additional site characterization to identify source areas and update CSM, as needed. • Modify the design of the injection well network. • Evaluate implementing an alternate technology.
The radius of influence is limited.	• The hydraulic conductivity is too low for effective treatment • An insufficient volume of AC was injected.	• Distribution of the AC and amendments will be limited.	• Increase the volume of AC injected. • Increase the injection pressure (in low permeability layers). • Inject additional AC using a tighter grid spacing. • Evaluate the use of an alternate technology.
The contaminant concentrations rebound after treatment.	• The injection wells are improperly located. • AC distribution was inadequate or was not emplaced in high contaminant mass zones. • An upgradient source remains untreated. • Matrix back-diffusion is occurring. • The AC may be saturated, or competitive adsorption is occurring where one contaminant may be displacing another from the AC.	• Remedial goals cannot be achieved. • The cost to achieve goals will increase. • Contaminants may have been mobilized to other parts of the site during injection, which previous had no or lower levels.	• Review the data collected during the injection (depth, pressures) and compare it to CSM. Additional (multiple) injections may be needed. • Evaluate the use of alternate technologies.
Surfacing ("daylighting") of AC occurs.	• Groundwater table is shallow. • Injection flowrate and/or pressure is too high. • Wells/injection points are poorly sealed.	• May increase time required to complete injections. • Results in uneven distribution of AC.	• Reduce injection pressure and flowrate of AC. • Increase or control the depth of groundwater by temporary pumping.
AC migrates to performance monitoring wells after injection.	• Injection flowrate and/or pressure is too high. • Injection radius of influence is greater than expected. • Preferential flow paths exist between the injection points and the monitoring wells.	• Performance monitoring data may be unreliable if AC is present within the well.	• Redevelop monitoring well. • Reinstall a new performance monitoring well if AC continues to migrate to the well after redevelopment.

12.0 ENHANCED IN-SITU BIOREMEDIATION

12.1 System Description

EISB encompasses a group of technologies that increase the growth of microorganisms to enhance biodegradation of organic compounds in the saturated zone. Depending on the target contaminants of concern, multiple bioremediation processes may be employed, including aerobic, anaerobic, and cometabolic pathways.

- Enhanced aerobic bioremediation is the process of stimulating indigenous oxygen-dependent microorganisms in soil and groundwater to create the conditions necessary for the microorganisms to biotransform contaminants of concern to innocuous byproducts. Aerobic bioremediation of petroleum hydrocarbons and other organic compounds, such as some fuel oxygenates (e.g., methyl tertiary-butyl ether [MTBE]), has been well studied and demonstrated (FRTR, 2020).
- Enhanced anaerobic reductive dechlorination is the process of modifying chemical, physical, and biological conditions in the aquifer to stimulate the microbial degradation of contaminants under anaerobic conditions to harmless end products (e.g., carbon dioxide or ethene). It is used to remediate CVOCs (e.g., TCE) and certain pesticides and other chlorinated organic contaminants (FRTR, 2020).
- Cometabolic bioremediation breaks down a contaminant utilizing an enzyme or cofactor that is produced by microbes oxidizing or reducing other compounds (metabolites) for energy and carbon. It may occur aerobically or anaerobically, but aerobic cometabolism is much more commonly used (FRTR, 2020).

Site-specific pilot studies coupled with results from microbiological tools (MBTs) are typically used to determine the technical feasibility and collect the site-specific information for design parameters, such as the amount of nutrients required, and the type of electron donor or electron acceptor amendments needed to enhance the targeted in-situ bioremediation process. While microcosms were used in the past to validate the applicability of a technology, MBTs are used today as they are less expensive than microcosms and have a quick turnaround time. Depending on the remedial action timeframes and MBT results, bioaugmentation may be used at some sites to either bolster or provide the microbial population necessary for the biological process.

Figure 12-1 illustrates a typical EISB system using groundwater recirculation. In the example, groundwater is removed using extraction wells, amended with nutrients and other electron donors or acceptors, as necessary, and re-injected upgradient of the contaminant plume. Injection wells or, in some cases, infiltration trenches are used to re-inject the water. The system operates as a closed loop and water is recirculated until cleanup levels are achieved. Extracted water that is not re-injected is treated and discharged. Treatment options for extracted water are presented separately in Section 18. Various types of other delivery mechanisms can also be used, including dual vertical well recirculation, horizontal well recirculation, combinations of well-infiltration trench recirculation, direct liquid amendment injection using wells or direct push technology, pneumatic and hydraulic fracturing, gas amendment injection, and pass-through or reactive cell designs.

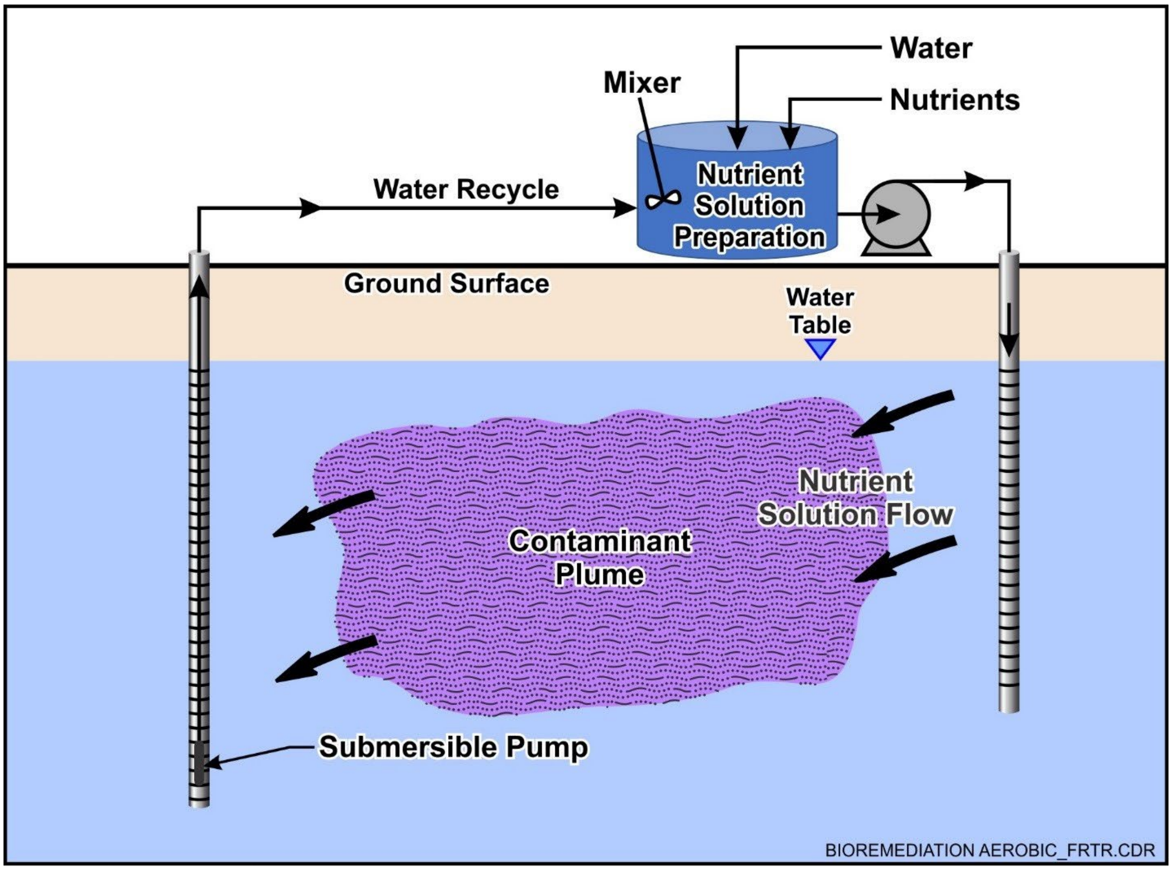


Figure 12-1. In-Situ Bioremediation System (FRTR, 2020)

The major biological processes by which contaminants are degraded include the following:

- **Aerobic Oxidation (oxygen respiration) –** This is the most effective mode for bioremediating petroleum constituents and other nonhalogenated organic compounds and involves the introduction of oxygen into the saturated zone to maintain an aerobic environment. Enhanced aerobic oxidation can be used to remediate contaminants dissolved in groundwater and sorbed to the aquifer matrix. Common methods for introducing oxygen are sparging air through injection wells (biosparging); injecting water saturated with air; and emplacing oxygen release compound (ORC®) in wells or trenches or directly injecting it using direct push technology. Biosparging is a variation of air sparging, which was addressed in Section 4. Bioventing, discussed in Section 5, is an in-situ bioremediation technology that is applicable to petroleum constituents in the unsaturated zone.

  Other classes of compounds are also amenable to treatment via aerobic oxidation; however, the level of effectiveness is highly dependent on the specific compounds being treated. For example, aerobic oxidation can be used to treat some halogenated compounds, such as VC and pentachlorophenol, but not for others such as TCE. In all cases, oxygen is utilized as the electron acceptor and the organic contaminants are used as a food source (electron donor) by the microorganisms that gain energy and carbon from biodegradation of the contaminants. The organic contaminant is converted into carbon dioxide, water, and microbial cell mass through the biodegradation process.

- **Anaerobic oxidation** – In anaerobic oxidation, the organic contaminants are used as the food source (electron donor) by the microorganisms. However, inorganic compounds other than oxygen serve as the electron acceptors (e.g., nitrate, sulfate). Amendments containing soluble sulfate, such as magnesium sulfate, can be added to the treatment area to stimulate sulfate-reducing conditions and help microbes metabolize compounds such as BTEX, simple polycyclic aromatic hydrocarbon (PAHs) such as naphthalene, and cyclic PAHs (NAVFAC, 2018a).
- **Anaerobic Reductive Dechlorination** – A hydrogen source consisting of either H_2 or a dissolved biodegradable carbon source like lactic acid, molasses, or a slow release formulation like hydrogen release compound (HRC®) is injected under pressure to initiate the step-wise replacement of chlorine atoms by hydrogen atoms. Microorganisms use the chlorinated solvents as electron acceptors in halorespiration and may also cometabolize the chlorinated solvent (NAVFAC, 2015b). Reductive dechlorination/halorespiration is more effective on the highly chlorinated solvents but will be effective to some degree on most chlorinated solvents.
- **Cometabolic Degradation** – Occurs when microorganisms using one compound as an energy source fortuitously produce an enzyme that chemically transforms another compound (i.e., contaminant of concern). As a result, organisms can degrade a contaminant without gaining any energy from the reaction. Cometabolic degradation may occur aerobically or anaerobically (NAVFAC, 2018a).

12.2 Performance Plots

Successful design and application of an EISB remedy begins with a detailed understanding of the CSM. The CSM should include up-to-date knowledge of geochemical and lithologic characteristics of the site, flow, and mass transport, and information related to the transformation and retardation of contaminants of concern and proposed amendments (NAVFAC, 2018a). Technology performance may be negatively impacted if the CSM and EISB design are not fully developed.

A comprehensive monitoring program helps to demonstrate successful performance of EISB. Performance monitoring is conducted after the amendments are added to gauge the progress of the remedy toward achieving remedial goals and to determine if additional application of amendments or a transition to an alternative technology would be beneficial. Parameters such as pressures, volumes, and flowrates can be measured in recirculation or injection systems to monitor system operation. Groundwater parameters can be monitored to track distribution and supply of electron acceptor amendments (e.g., DO, nitrate, sulfate) and electron donor amendments (e.g., total organic carbon) to ensure suitable aquifer conditions are maintained for treatment by the targeted biodegradation processes (NAVFAC, 2018a). Figure 12-2 shows an example plot of dissolved oxygen distribution over time.

The effectiveness of EISB systems in restoring groundwater quality should be evaluated by plotting contaminant concentrations measured in monitoring wells over time. During in-situ bioremediation, the concentration of constituents measured in groundwater will decrease until an asymptotic level is reached. A typical performance plot for reductive dechlorination is shown in Figure 12-3. The figure shows the trend in molar concentrations of parent and daughter compounds in groundwater samples collected from a monitoring well at various times after EISB was implemented. The proportion of the compounds should change over time in a successful application of EISB. In Figure 12-3, the concentration of TCE decreases while that of ethene increases. Intermediate compounds such as cis-1,2-DCE and VC first increase in concentration before decreasing.

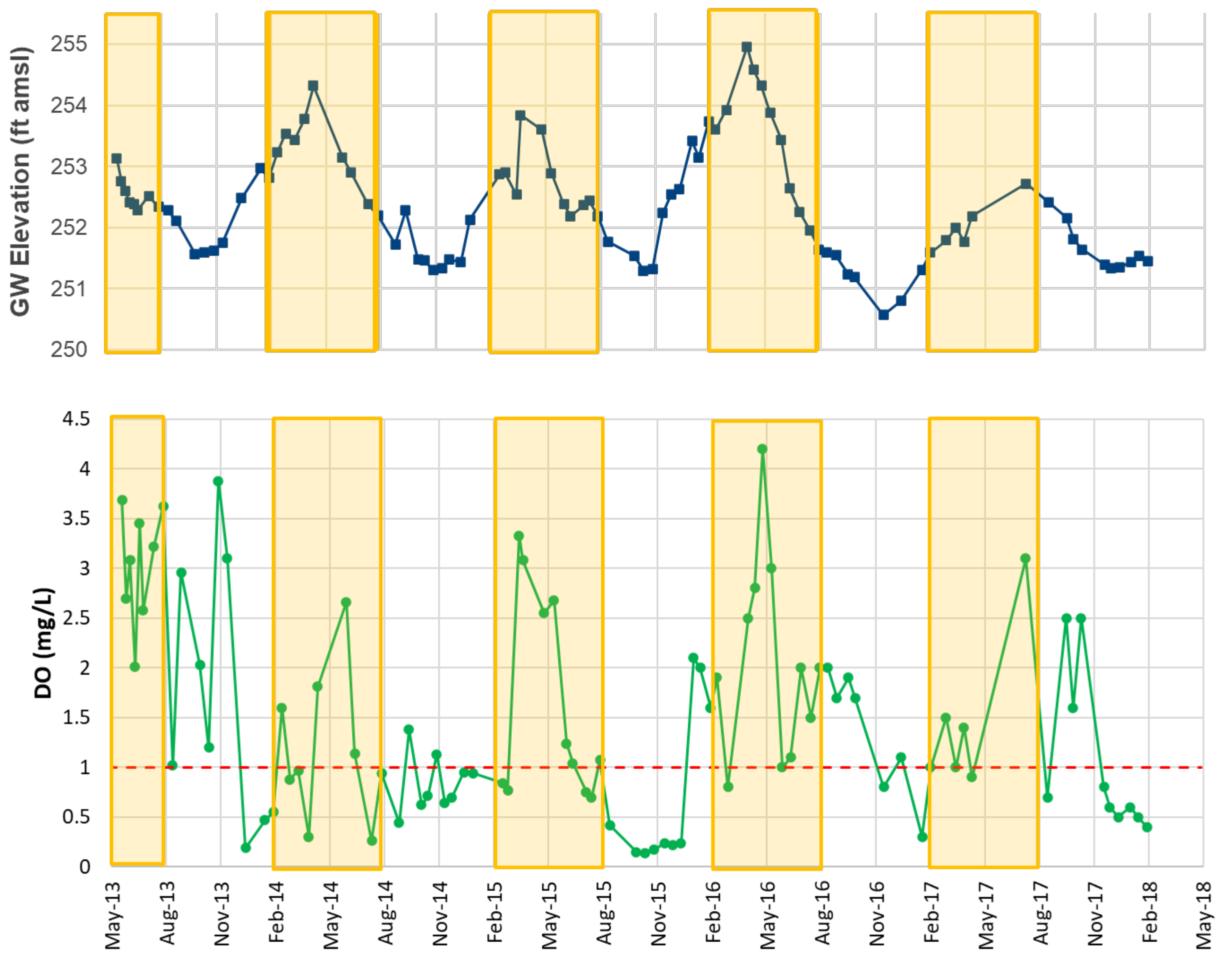


Figure 12-2. Bioremediation System (Biosparge) Monitoring at NAS Meridian

Example: *DO concentrations were monitored to evaluate the effectiveness of electron acceptor distribution during operation of a biosparge system at Building 228, NAS Meridian. A minimum DO concentration of 1.0 mg/L was targeted to ensure suitable aquifer conditions for aerobic bioremediation of BTEX. After the first year of operation, decreased DO concentrations were observed, particularly during the fall and winter months when the water table was seasonally* *lower. System operation was modified by shortening the pulsed (on/off) operating cycle to reduce preferential pathways that may have developed and improve DO distribution. Further monitoring suggested that the limited saturated zone observed during the fall and winter months resulted in less effective DO distribution. Based on this, seasonal operation of the system was recommended as a further optimization strategy.*

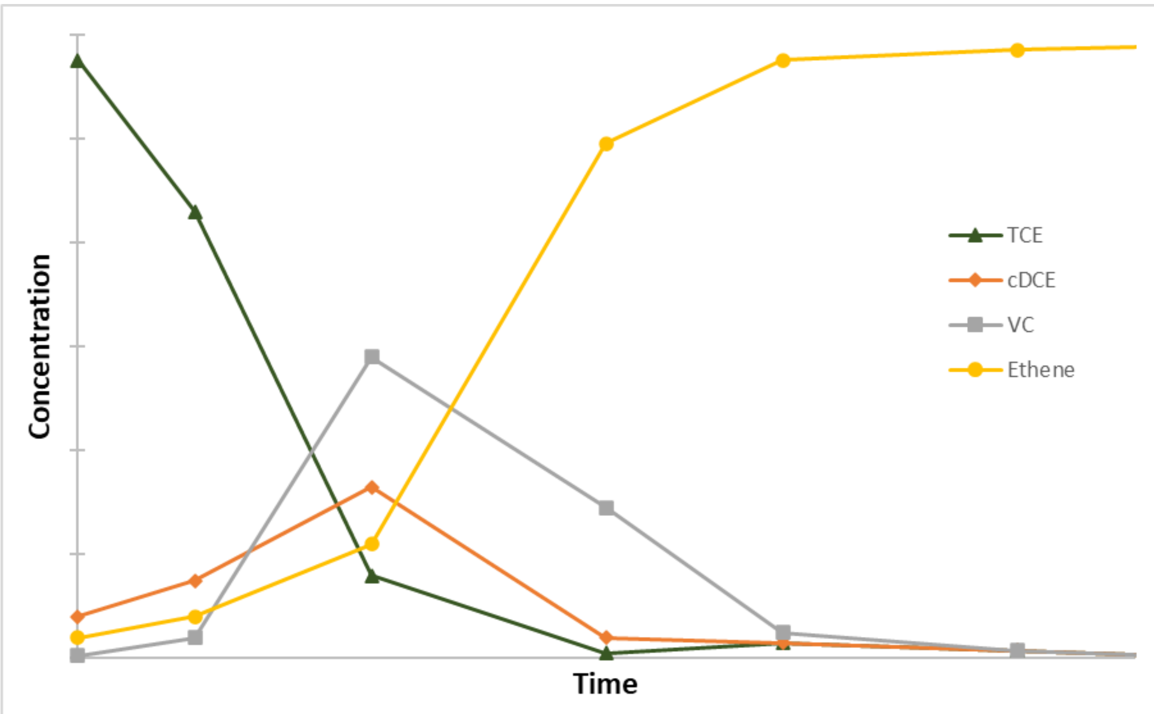


Figure 12-3. Performance Plot of a Typical In-Situ Bioremediation System for Chlorinated Compounds

12.3 Common Operational Problems

Provided treatability studies have previously verified that the technology is appropriate for the site conditions, performance problems with EISB systems are generally related to microorganism growth requirements and the supply of electron acceptors, electron donors, or nutrients. The nature of the problems may vary from deficiencies in the amount of amendments to fouling of the injection points. Table 12-1 lists problems common to EISB systems, in general. Table 2-1 should also be consulted to identify hydraulic containment problems potentially associated with closed loop systems that re-circulate groundwater.

12.4 Common Optimization Recommendations

Optimization recommendations for EISB systems should focus on ensuring that electron acceptor, electron donor, and nutrient levels are not rate limiting and that the delivery system is operating efficiently. The more common recommendations include increasing amendment addition to ensure favorable oxidation-reduction conditions, pulsing the injection of nutrients to minimize biological fouling, or rehabilitating well screens that do become fouled. In some cases, the necessary microorganisms may not be present to allow complete biodegradation. This can be determined by the use of MBTs. The lack of necessary organisms can be addressed through the addition of an appropriate microorganism or microbial culture known to degrade the contaminant of concern present at the site. This is referred to as bioaugmentation. However, should asymptotic levels persist, continued operation of the in-situ bioremediation system will generally not produce additional reduction in concentrations. In this case, if further remediation is necessary, implementing either another technology or MNA should be considered. Table 12-1 provides guidance on optimizing EISB systems. For closed loop systems that re-circulate groundwater, additional recommendations for optimizing hydraulic control are included in Table 2-1.

Table 12-1. Common Operational Problems and Optimization Strategies of In-situ Bioremediation Systems

Operational Problem	Potential Causes	Potential Negative Impacts on Performance	Optimization Strategy
The contaminant concentrations have not declined in the system influent and in the monitoring wells.	• Source areas or hot spots have not been adequately controlled.	• The presence of a continuing source of contaminants will prevent cleanup goals from being achieved.	• Identify and remediate source areas and hot spots including excavation, if feasible. • Evaluate the use of alternate technologies, such as physical removal of LNAPL.
The treatment zone is insufficient or not as predicted.	• The soil permeability is lower than estimated. • The number of injection points is not adequate or they are improperly located.	• Amendments and nutrients will not reach all contaminants and cleanup goals will not be achieved.	• Install additional wells and/or enlarge the infiltration galleries.
Contaminant degradation is slow or incomplete.	• The delivery of substrate, nutrients, microbial cultures, or other amendments is not sufficient to maintain biodegradation rates. • The pH of the groundwater is not between 6 and 8. • Redox conditions are not favorable for the biodegradation process. • For aerobic oxidation, oxygen distribution to the contaminated zone is not sufficient to maintain a residual concentration above 1 mg/L. • For anaerobic reductive dechlorination, an overabundance of competing electron acceptors is present and inhibits biodegradation rates. • Deficiencies of inorganic nutrients such as nitrogen and phosphate may inhibit microorganism growth. • Low solubility constituents are not bioavailable. • Preferential channels are formed by systems that inject amendments causing most of the contaminants to be bypassed. • For anaerobic reductive dechlorination, the microbial population may require a longer than anticipated time to adjust to new conditions and to create subsurface	• Biodegradation rates slows and cleanup will be incomplete or will take longer than estimated.	• Increase the rate of injection or evaluate the need for additional wells and/or infiltration galleries. • Utilize MBTs and other monitoring data to evaluate the need for additional or different substrate, nutrients, microbial cultures, or other amendments. • Evaluate the use of alternate technologies including MNA. • Pulse the injection wells to minimize effects of preferential channels.

Table 12-1 (continued). Common Operational Problems and Optimization Strategies of In-situ Bioremediation Systems

Operational Problem	Potential Causes	Potential Negative Impacts on Performance	Optimization Strategy
	conditions conducive to contaminant biodegradation.		
The contaminant concentrations in the system influent and in the monitoring wells have reached asymptotic levels and/or rebound to higher levels when pumping is terminated.	• Remediation may only be occurring in the more permeable units comprising the aquifer. •Matrix diffusion or back diffusion may be contributing to contaminant rebound.	• The inability to distribute nutrients and amendments to low permeability zones will extend cleanup time or prevent achieving cleanup goals.	• Evaluate the use of alternate technologies, including MNA. • Consider the use of fracturing to allow better distribution of amendments into lower permeability zones. • Optimization of injection methods is further discussed in Section 16.
Increasingly higher pressure occurs in the reinjection wells and/or infiltration galleries.	• The wells and/or infiltration galleries have become plugged through mineral encrustation or biological fouling.	• Organic substrate, electron acceptors, or other amendments will not reach contaminants and cleanup will not be achieved or will take longer than estimated.	• Mechanically rehabilitate affected wells and/or trenches. • Perform routine cleaning and surging of the wells and/or trenches to prevent future mineral encrustation and biofouling. • Install a filtration system to remove biomass and particulates. • "Pulse" nutrients into the subsurface to discourage biofouling. • Replace the affected wells and/or trenches that cannot be rehabilitated.
The contaminant plume expands during the operation of a liquid delivery system.	• The extraction well pumping rates are not sufficient to re-circulate groundwater within the treatment zone. • The number or placement of the extraction wells is not adequate.	• Failure to re-circulate groundwater will allow the plume to enlarge in size and potentially reach receptors. The larger area will also result in increased remediation time and require expanding the bioremediation system.	• Increase the pumping rates at the extraction wells. • Install additional extraction wells. • Expand the bioremediation treatment zone to include the impacted area.

13.0 IN-SITU CHEMICAL OXIDATION

13.1 System Description

ISCO is an in-situ remediation treatment technology used to treat soil and groundwater contaminated with organic compounds. Chemical oxidation of organic contaminants is achieved by injecting oxidizing chemicals into the contaminated soil and/or aquifer through injection wells or temporary points. The chemicals are then distributed through the affected system by dispersion and diffusion. A discussion of injection technologies for in-situ treatments in provided in Section 17. The chemical oxidation process rapidly transforms organic contaminants into less harmful degradation products. The primary components of a typical ISCO system are shown in Figure 13-1. Design issues related to ISCO systems are discussed in the NAVFAC technical memorandum, *Design Considerations for In Situ Chemical Oxidation* (NAVFAC, 2015c).

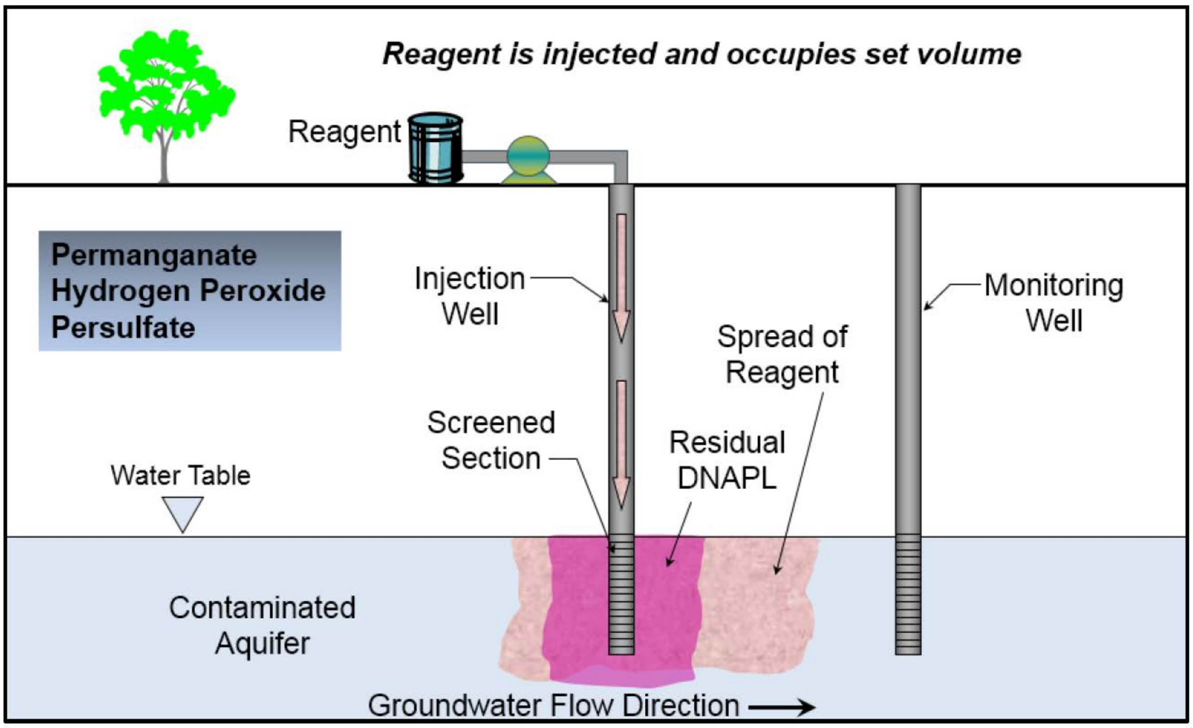


Figure 13-1. In-Situ Chemical Oxidation Treatment System (FRTR, 2020)

A variety of ISCO reagents are available on the market including hydrogen peroxide, sodium persulfate, potassium permanganate, sodium percarbonate, potassium permanganate, and sodium persulfate, which generally are applied in liquid form. Oxidants normally shipped in solid form, such as potassium permanganate or sodium persulfate, are dissolved easily and mixed on site to form a solution having the required design concentration (FRTR, 2020). A description of three most common ISCO processes is provided in the following paragraphs.

Fenton's Reaction – Hydrogen peroxide and ferrous iron catalyst are used to initiate the chemical oxidation process in Fenton's reaction, which are capable of reacting with a variety of contaminants of concern including chlorinated ethenes and petroleum hydrocarbon constituents.

Hydroxide and other radicals produced from the hydrogen peroxide and ferrous iron catalyst oxidize contaminants in an exothermic reaction. These radicals are strong non-specific oxidizers that transform the contaminants into carbon dioxide, water, and other byproducts. Residual hydrogen peroxide rapidly decomposes to water and oxygen in the subsurface environment, due to its unstable nature. The soluble iron catalyst added to the aquifer in trace quantities is precipitated.

Hydrogen peroxide is typically applied into the subsurface at concentrations of up to 20%. In a subsurface with minimal transition metals, hydrogen peroxide is typically supplemented with ferrous iron (Fe^{2+}) in an effort to stimulate radical generation. If the subsurface contains an overabundance of transition metals, hydrogen peroxide is usually supplemented with a stabilization agent intended to aid the subsurface persistence and distribution of the hydrogen peroxide. Several concerns that need to be addressed when using this process:

- Heat can be generated in the presence of a vigorous reaction of hydrogen peroxide in the subsurface. This can be mitigated by the addition of chemical stabilizers or inhibitors, or by simply reducing the concentration of the peroxide and/or rate of application. In some cases, these exothermic characteristics can be beneficial, if sufficiently controlled, to enhance desorption and dissolution of sorbed and NAPL mass, if present.
- Temporary changes in the subsurface geochemistry (pH, DO, and oxidation reduction potential) can result in the mobilization of metals in the treatment area. In most cases, these changes do not persist as the geochemical conditions return to baseline.
- There is a limited potential for volatilization of contaminants from groundwater to soil gas phase due to changes in subsurface temperature and the evolution of gas during the decomposition of hydrogen peroxide.

Permanganate Oxidation – Permanganate oxidation uses potassium permanganate or sodium permanganate to initiate the oxidation reaction. Permanganate oxidation is applicable in environments not as favorable for Fenton's reaction, such as areas characterized by low permeability soil where a slower and longer reaction time is beneficial. Unlike Fenton's reaction, permanganate acts as a metal-oxo reagent and does not rely on generation of a hydroxyl radical to oxidize organic contaminants.

The ability for most natural aquifer materials to consume permanganate reduces concern that the presence of permanganate in solution would emerge as a major contaminant problem at most sites. On the other hand, permanganate oxidation reaction can release metals (e.g., Cr^{3+}) to the aqueous phase at concentrations that may be of regulatory concern. Other key reaction products include manganese dioxide and carbon dioxide. Another concern associated with the use of permanganate is that it can cause the groundwater to turn purple. This is a particular concern at sites where the aquifer is in close proximity to an open water body or where there is a concern of exceeding secondary groundwater water quality standards.

Persulfate Oxidation – Persulfate is applied in the form of a salt, which dissociates in water to form the sulfate anion, $S_2O_8^{2-}$. The persulfate salts are available as ammonium persulfate, sodium persulfate, and potassium persulfate. However, ammonium persulfate is typically not applied in environmental applications due to the formation of ammonia and potassium persulfate and because of its low solubility in groundwater. Sodium persulfate is a yellow crystal having a solubility of about 40% in water at room temperature. It is more stable than hydrogen peroxide and has a high oxidation potential.[2] Although highly oxidizing, the reaction is kinetically slow. A number of methods are available to "activate" the persulfate to form the sulfate radical, SO_4^-, which has a much higher oxidation potential (2.6 V) than the sulfate anion, is kinetically fast, and is much more stable than the hydroxyl radical, allowing it to migrate greater distances in the aquifer. Methods commonly employed at environmental sites include the application of heat via steam, raising the pH of the aquifer through adding a base such as sodium hydroxide, adding peroxides such as calcium peroxide or hydrogen peroxide, and the addition of a ferrous salt to catalyze the reaction. The reaction mechanisms are complex and involve a number of chain-initiating, -propagating, and -terminating reactions.

13.2 Performance Plots

The effectiveness of ISCO treatment may be determined though performance plots. The data that should be collected for an ISCO treatment event are described below (NAVFAC, 2019b).

- Pre-injection sampling. Contaminant concentrations prior to chemical injection will provide the baseline for source reduction.
- Injection measurements. The injection pressures, flowrates, oxidant volume, and location of injections should be monitored throughout the injection. Groundwater quality measurements (e.g., pH, alkalinity, oxidation-reduction potential, and conductivity) and oxidant concentrations should also be monitored during the injection process to understand the changing site conditions and evaluate effectiveness of the oxidation distribution.
- Post-injection sampling. Contaminant concentrations after treatment will determine the reduction of the source area and identify any rebound effects. Oxidant concentrations should be measured as well to evaluate the persistence of the oxidant within the treatment zone and provide additional context for contaminant concentration data. Contaminant concentrations may be biased low if measurements are collected while oxidant is still present in the treatment zone, due to reaction occurring between the time of sample collection and analysis.

The data should be compared with remedial objectives and goals to determine the effectiveness of the ISCO treatment event. The data will also allow the RPM to assess the conditions to optimize subsequent treatment events.

Example: *ISCO using the Fenton's reagent method has been effectively used to remediate source areas of chlorinated solvents at the NAS Pensacola Former Industrial Wastewater Treatment Plant Sludge Drying Bed site. The remedial objective was to substantially reduce concentrations of chlorinated hydrocarbons in the source area to ensure natural attenuation would be an effective remedy. Initial concentrations of TCE historically exceeded 3,000 µg/L in the source area. After two phases of injection, TCE concentrations in the source area ranged from less than 1 µg/L to*

[2] The sulfate anion has an oxidation potential of 2.1 V compared to 1.8 V for hydrogen peroxide.

100 µg/L with no rebound – a reduction of more than 96%. The results of the ISCO treatment at NAS Pensacola are shown in Figure 13-2.

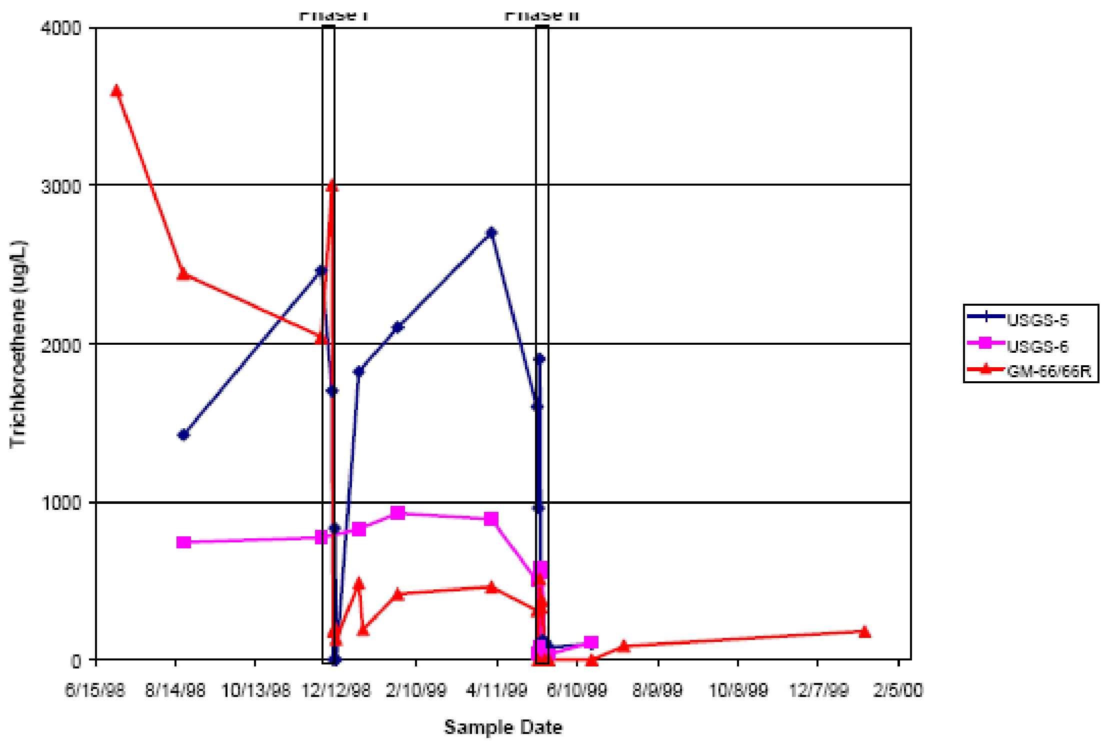


Figure 13-2. In-Situ Chemical Oxidation Treatment at NAS Pensacola

13.3 Common Operational Problems

Chemical oxidation treatments must be conducted under carefully controlled conditions. The existing site conditions must be evaluated to determine the appropriate use of this process. The effectiveness of ISCO is dependent on site conditions, treatment design, and the consideration of post-treatment effects. The two most critical success factors for ISCO treatment projects are the effective distribution of an adequate volume of reagent in the treatment zone and the reactivity of a particular oxidant with the contamination present. While there are differences in the applicability of the different chemical oxidation processes, the operational problems associated with these processes are similar. Common operational problems related to ISCO are provided in Table 13-1.

Caution should be used if considering ISCO for a site where PFAS may be present. At this time, chemical oxidants are not capable of complete degradation of PFAS. However, chemical oxidants may stimulate transformation of some PFAS compounds, referred to as precursors, into more stable end products such as perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS). In many cases, the end-product compounds are more mobile in groundwater, and potentially more toxic, than the precursor compounds from which they were formed (NAVFAC, 2019b).

13.4 Common Optimization Recommendations

Optimization strategies typically cannot be applied during a chemical oxidation treatment event; instead, optimization strategies focus primarily on correcting operational problems for subsequent treatment events. Optimization problems resulting from most site condition limitations will require the use of a modified injection method or an alternative technology. Other optimization recommendations include design modifications (e.g., increased oxidant volume, increased injection pressure, modify injection well design) and the combined use of technologies. Common optimization strategies for ISCO are provided in Table 13-1.

Table 13-1. Common ISCO Operational Problems and Optimization Strategies

Operational Problem	Potential Causes	Potential Negative Impacts on Performance	Optimization Strategy
Contaminant removal is not complete.	• Too much contamination is present for effective treatment. • An insufficient volume of chemical reagent was injected. • The reaction proceeds too rapidly due to the presence of a naturally high concentration of catalysts. • The injection wells are improperly located. • The aquifer material interferes with the reaction. • Preferential pathways prevent adequate distribution of reagents.	• Oxidation of the contaminants will be incomplete. Remedial goals may not be achieved. • The chemical reagents will not reach the contaminants. • The reaction rate is slowed or the chemical reagents are consumed by the aquifer material.	• Increase the volume of chemical reagents injected. • Modify the design of the injection well network. • Perform multiple rounds of ISCO reagent injection. Multiple injections are not uncommon for ISCO. Performance monitoring data can be used to guide future injections to focus efforts on the remaining hot spots. • Evaluate implementing an alternate technology. • Perform additional site characterization. • Modify the injection technique (direct injection, recirculation, push-pull). Optimization of injection methods is further discussed in Section 16. • Perform bench-scale treatability tests to measure soil oxidant demand and fine-tune dosing based on results.
The radius of influence is limited.	• The hydraulic conductivity is too low for effective treatment. • An insufficient volume of chemical reagent was injected. •The reaction proceeds too rapidly due to the presence of a naturally high concentration of catalysts. •The aquifer material interferes with the reaction and consumes the reagents. • The reaction forms byproducts, which may clog the porous media and well screens.	• Distribution of the chemical reagents will be limited. • Oxidation of the contaminants will be incomplete. • The byproducts will cause plugging, create preferential pathways and divert flow.	• Increase the volume of oxidant injected. • Inject additional chemical reagents to inhibit reaction catalyst. • Modify the injection technique (direct injection, recirculation, push-pull). Optimization of injection methods is further discussed in Section 16. • Evaluate the use of an alternate technology. • Perform bench-scale treatability tests to measure soil oxidant demand and fine-tune dosing based on results
The contaminant concentrations rebound after treatment.	•The injection wells are improperly located. • Exothermic reaction effects • An upgradient source remains untreated. • Back-diffusion is occurring. • Mounding and mobilization of the contaminants is occurring.	• Remedial goals cannot be achieved. • The cost to achieve goals will increase. • Contaminants could be mobilized to other parts of the site, which previous had no or lower levels	• Modify the system design. • Use chemical oxidation in combination with other technologies. • Perform multiple injections of the ISCO reagents. Multiple injections are not uncommon for ISCO. Rebound can be used

Table 13-1 (continued). Common ISCO Operational Problems and Optimization Strategies

Operational Problem	Potential Causes	Potential Negative Impacts on Performance	Optimization Strategy
			to guide future injections to focus efforts on the remaining hot spots. • Use recirculation to achieve better hydraulic control.
Surfacing ("daylighting") of reagent occurs	• Large volume of gas generated while using hydrogen peroxide. • Groundwater table is shallow. • Injection flowrate is too high. • Wells/injection points are poorly sealed.	• May increase time required to complete injections. • Result in uneven distribution of oxidant.	• Reduce concentration and/or flowrate of oxidant. • Install a vapor recovery system (if necessary for peroxide applications). • Use a recirculation approach. If recirculation is being used, increase extraction flowrates and decrease injection flowrates.

14.0 IN-SITU CHEMICAL REDUCTION

14.1 System Description

ISCR is the in-place abiotic transformation of contaminants by chemical reductants. Chemical reduction may be preferred over chemical oxidation at sites with naturally reducing conditions. ISCR is used for soil and/or groundwater remediation and can treat dissolved contaminants as well as halogenated DNAPLs. Contaminants treated by ISCR typically include chlorinated compounds, metals in a high oxidation state (e.g., hexavalent chromium or Cr^{6+}), explosives, and oxidized inorganics (e.g., perchlorate). Commonly used chemical reductants include ZVI, zero valent zinc (ZVZ; a stronger reductant that ZVI), iron minerals, bi-metallic materials, polysulfides, dithionite, as well as other commercial materials such as furnace slag or iron scrap (FRTR, 2020).

The long-term treatment impacts associated with injection of chemical reducing media make this technology well suited for applications in PRBs. More details regarding PRBs are provided in Section 10. ZVI (granular, micro [m-], and nano [n-] scale) is the most common ISCR amendment and can be placed into the subsurface by a variety of methods. These include excavation and backfill, trenching, soil mixing, direct push technology (DPT) injection (mZVI and nZVI), and hydraulic/gravity feed delivery to conventional injection wells (nZVI). Two common approaches to applying ISCR treatment are shown in Figure 14-1. The delivery method is specific to ZVI particle size, treatment scenario (source or plume treatment), and subsurface lithology (NAVFAC, 2020). Section 17 includes a discussion of various injection methods.

ZVI in groundwater corrodes continuously via reaction with water and organics, both under oxic and anoxic conditions. This process reduces its reactivity and capacity over time. While the reactivity of granular ZVI can last multiple decades depending on aquifer geochemistry, the reactive longevity of mZVI and nZVI is shorter due to their smaller particle diameters and higher reactive surface areas. Sulfidation of ZVI, activated carbon-ZVI composite amendments, and formulations of food-grade emulsified vegetable oil with ZVI (eZVI) are recent advances in amendment composition to improve reactive longevity and mobility in the subsurface (NAVFAC, 2020).

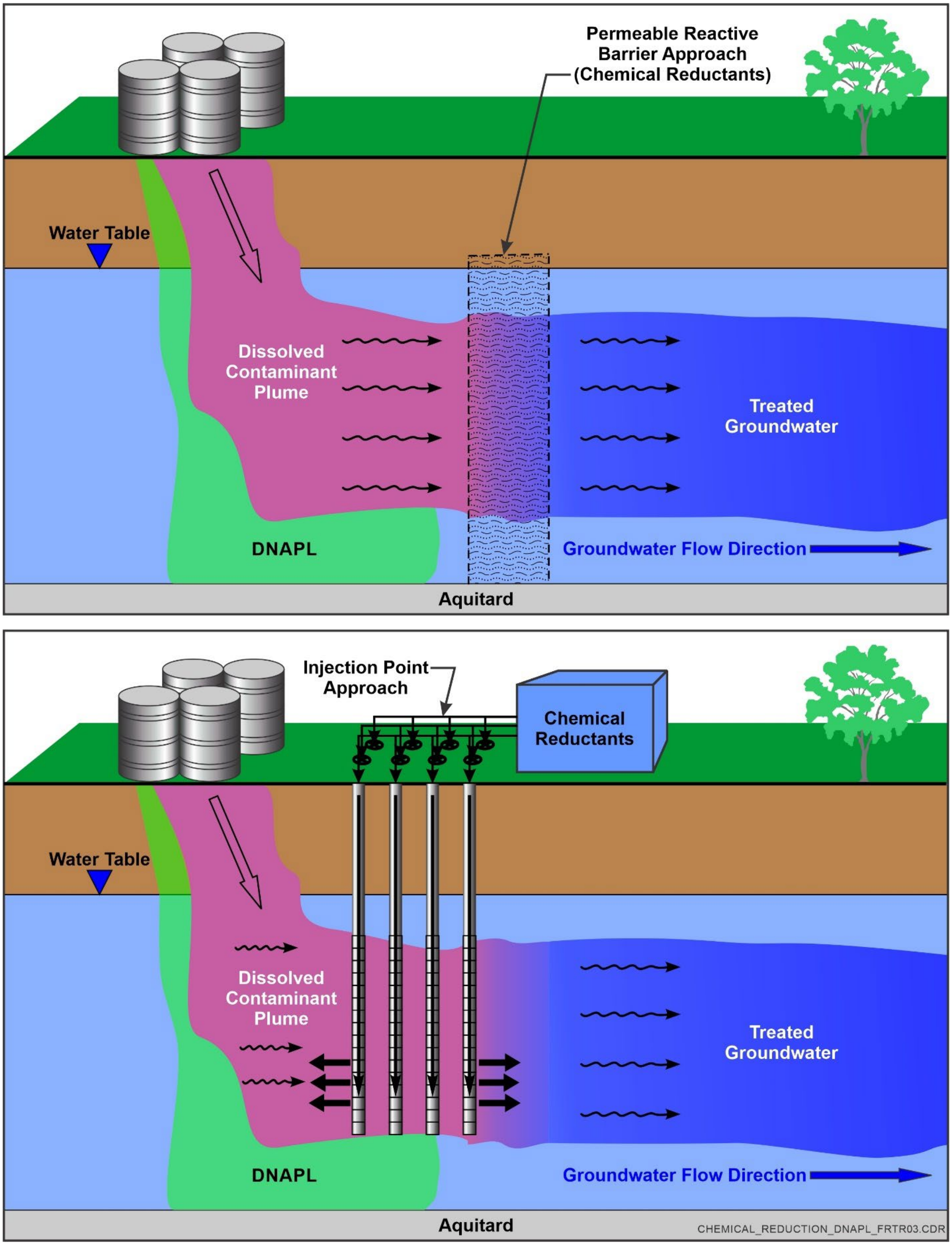


Figure 14-1. In-Situ Chemical Reduction Treatment System (FRTR, 2020)

Several variations of ISCR technologies have been established and continue to emerge as innovative treatment approaches (FRTR, 2020).

- **Combined ISCR and in-situ bioremediation** – Hybrid amendments that combine ZVI emulsified in a carbon substrate are frequently used to treat chlorinated compounds, which create strong reducing conditions to drive chemical reduction while also supporting reductive dechlorination. In such an application, the ZVI slurry can be bioaugmented with a dechlorinating bacterial culture to further enhance the reductive dechlorination process.
- **In-situ biogeochemical transformation (ISBGT)** – ISBGT is an emerging mechanism for the degradation of chlorinated ethenes in the subsurface. The term biogeochemical transformation is used because a combination of biological and abiotic processes is responsible for the transformation. The contaminant is degraded by abiotic reactions with minerals such as iron sulfide that are produced by the action of microorganisms in the subsurface (both naturally occurring minerals and those formed through the injection of treatment reagents). Iron and sulfate reducing organisms obtain electrons from organic matter and transfer these electrons to iron oxide minerals reducing them to iron sulfide. The iron sulfide then reacts with chlorinated compounds abiotically, transforming them to nonchlorinated products such as acetylene ethene, ethane and organic acids. Microbial degradation of the nonchlorinated organic products yields carbon dioxide as the ultimate transformation end product (FRTR, 2020).

14.2 Performance Plots

An adequately designed monitoring program should be developed to evaluate the long-term effectiveness of ISCR treatment. Baseline conditions should be compared to changes over time after ISCR implementation, and conditions upgradient, within, and downgradient of the treatment zone should be monitored. The following parameters should be included in a performance monitoring program (NAVFAC, 2020):

- Contaminant concentrations, including parent and degradation products,
- Aqueous geochemical indicators (e.g., oxidation reduction potential, total organic carbon, pH, sulfate, and ferrous iron),
- Mass flux reductions, and
- Biogeochemical and reactivity characterizations of aquifer materials. For example, the formation of iron sulfide after ZVI injection may stimulate in-situ biogeochemical transformation of contaminants, or high concentrations of nitrate, carbonate, and silica may passivate ZVI over the long term.

The data should be compared with remedial objectives and goals to determine the treatment effectiveness. The data will also allow the RPM to assess the conditions to optimize subsequent treatment events.

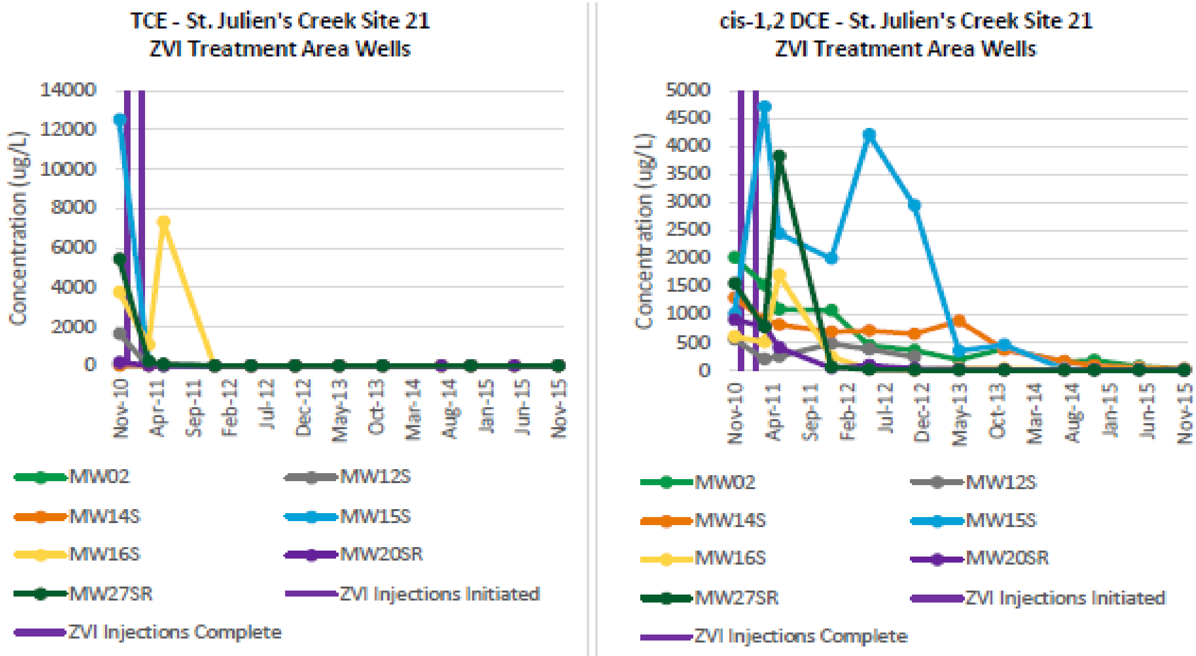


Figure 14-2. ISCR Treatment at St. Julien's Creek Annex Site 21 (NAVFAC, 2018b)

Example*: At St. Julien's Creek Site 21, 85,850 pounds of ZVI were injected into 202 temporary direct push points over a total treatment area of 18,500 square feet. ZVI was mixed with water to create a ZVI/water slurry to facilitate injection. Areas of the plume not treated with ZVI were treated with emulsified vegetable oil (EVO) to stimulate reductive dechlorination. Time series plots show that ZVI injections were very effective in reducing all chlorinated VOCs to levels at or near maximum contaminant levels in all monitoring wells within the ZVI treatment areas. An overall 96% reduction in total VOCs was observed. These charts suggest that while some degree of abiotic reactions may be occurring to reduce TCE concentrations, other processes, such as reductive dechlorination also appear to have occurred. Well MW15S in particular showed the greatest concentrations of reductive dechlorination daughter products, and dechlorination reactions continued over the 5 year post-injection monitoring period (NAVFAC, 2018b).*

14.3 Common Operational Problems

The possibility of remobilizing source contamination is always a concern when investigating for and treating contamination, particularly when DNAPL is present. When implementing ISCR injections at a site where DNAPL is present, precautions should be taken to anticipate and prevent the remobilization of DNAPL that may result in more difficult attempts at remediation (NAVFAC, 2020).

If reactive media will be placed using injection methods, soil properties that affect the propagation of the reactive materials should be assessed to ensure proper placement of the reactive material. Amendment injection methods for implementation of in-situ remedies are further discussed in Section 16. ISCR reagents may have a very long lifetime in the subsurface; however, the reduction reaction will stop when the reaction capacity is fully utilized. Batch and column treatability tests with site groundwater are recommended to determine the maximum removal capacity before implementation (ITRC, 2011).

Long-term treatment effects of ISCR can be negatively impacted by ZVI passivation due to corrosion and subsequent geochemical precipitation (e.g., siderite). Certain constituents, such as nitrate or silica, also strongly passivate ZVI. The degree of passivation varies depending on the site-specific geochemical conditions, and in the case for PRBs, can have significant effects on performance by reducing the hydraulic conductivity of the barrier and altering the direction of groundwater flow. Biogeochemical conditions within and around the treatment area should be evaluated prior to design and the barrier should be refreshed every few years to ensure effective treatment in the long-term (NAVFAC, 2020).

Common operational problems related to ISCR are provided in Table 14-1.

14.4 Common Optimization Recommendations

Optimization strategies typically focus primarily on the design of the initial ISCR treatment application and then on correcting operational problems for subsequent treatment events to the extent possible. Batch treatability tests are a useful and cost-effective way to screen reactivity of different ZVI products. Flow-through column tests that simulate groundwater flow in the field are preferred as they provide more robust design information.

Remediation problems resulting from most site condition limitations (e.g., inadequate subsurface distribution due to site specific geology) may require the use of a modified injection method or alternative technology. For PRB- and injection-based technologies, highly impermeable materials such as clay and bedrock matrix will limit the success of ISCR or require the use of permeability enhancement techniques such as hydraulic or pneumatic fracturing (FRTR, 2020). Other optimization recommendations include the combined use of technologies. Common optimization strategies for ISCR are provided in Table 14-1.

Table 14-1. Common ISCR Operational Problems and Optimization Strategies

Operational Problem	Potential Causes	Potential Negative Impacts on Performance	Optimization Strategy
Contaminant removal is not complete.	• An insufficient volume of amendment was injected. • The injection wells are improperly located. • Injection of the ISCR amendment impacts hydraulic conductivity within the treatment zone.	• Remedial goals may not be achieved. • Contaminants will not come into contact with the ISCR amendment.	• Conduct batch and/or flow-through column tests using the target amendment to estimate soil loading in the field. • Perform additional site characterization and revisit CSM to ensure appropriate injection well placement. • Modify the injection technique (e.g., use of hydraulic or pneumatic fracturing). Optimization of injection methods is further discussed in Section 16. • Evaluate implementing an alternate technology.
The radius of influence is limited.	• An insufficient amendment volume was injected. • The site-specific hydraulic conductivity is too low for effective treatment.	• Distribution of the amendments will be limited. • Treatment of the contaminants will be incomplete.	• Conduct batch and/or flow-through column tests using the target amendment to soil loading in the field. • Modify the injection technique (e.g., use of hydraulic or pneumatic fracturing). Optimization of injection methods is further discussed in Section 16. • Evaluate the use of an alternate technology.
Performance decreases over time.	• There is a loss of media reactivity due to passivation from adverse geochemical conditions. • There is a loss of porosity in the treatment zone as a result of mineral precipitates or biofouling.	• Cleanup goals will not be achieved. • Groundwater flow paths may be altered, limiting the long-term effectiveness of a PRB.	• Evaluate the need for additional applications of ISCR amendments. • Consider regeneration of ZVI media.
Arsenic is mobilized after injection of chemical reductants (e.g., calcium polysulfide)	• Naturally occurring arsenic is mobilized due to changed geochemical aquifer conditions following ISCR treatment.	• Arsenic is reduced from the less mobile As^{5+} to the more mobile (and toxic) As^{3+}. • Further treatment is required to address the increased arsenic concentrations in groundwater.	• Evaluate the aquifer geochemistry to determine if the arsenic will re-precipitate or form an immobile mineral downgradient of the injection location. • Conduct batch and/or flow-through column tests as part of the design process to evaluate the potential for metals to be mobilized following ISCR treatment. • Add iron (e.g., ferrous sulfate) in the treatment area to sequester the arsenic during ISCR treatment.

15.0 IN-SITU THERMAL TREATMENT

15.1 System Description

In-situ thermal treatment technologies involve enhancing the movement of highly viscous fluids and/or enhancing the volatilization of VOCs so that they can be more readily removed by groundwater or vapor extraction. This section focuses on a discussion of thermal heating technologies, and the operation of vapor extraction systems is further discussed in Section 3. Thermal treatment is more commonly applied to treatment of vadose zone soils because of the energy needed to heat large volumes of water in the saturated zone; however, successful application of thermal treatment in the saturated zone has also been documented.

Thermal treatment to enhance the movement of viscous fluids can be implemented at low temperatures (<100°C) using steam injection wells, hot water flooding, or in-situ steam generation by electrical resistance heating. Thermal treatment to mobilize free product and enhance volatilization of VOCs typically heats the subsurface using electrical current or the direct application of heat to raise the subsurface temperature above the volatilization temperature of the contaminants being treated. The three technologies currently used are electrical resistance heating (ERH), thermal conductive heating (TCH), and steam enhanced extraction (SEE). A description of each thermal treatment system follows.

Steam Enhanced Extraction – SEE may be applied to contaminated soils using a fixed system of wells or augers for steam injection. The injection of low-moisture steam heats the formation to enhance and control contaminant mobility. The injected steam creates a pressure gradient, and the heat reduces the viscosity and density of the organic contaminants. The flow of the injected steam displaces and mobilizes NAPLs toward the extraction wells (FRTR, 2020). Steam, water, vapors, and any NAPL are collected in multi-phase extraction wells (see Section 6 for further discussion of MPE). The primary components of a typical steam injection treatment system are shown in Figure 15-1.

Electrical Resistance Heating – ERH uses an electrical current to heat an aquifer so that water and chemicals trapped in conductive regions are volatilized and ready for vacuum extraction. During ERH application, an electric current is passed into the subsurface through vertical, angled, or horizontal electrodes in a three-phase triangular or a six-phase hexagonal structure (i.e., six-phase heating). Electrodes are generally installed in the subsurface soil matrix through conventional drilling techniques that are used to install monitoring wells. Electric current is conducted through the moisture present in the subsurface soil where the resistance it encounters leads to heating of the subsurface. This heating increases the subsurface temperature, resulting in the volatilization of chemicals from the groundwater. During electrical resistance heating, the ground surface is covered by an insulating vapor barrier. The volatilized chemicals are then vacuum-extracted by an SVE system installed above ground. The primary components of a typical ERH system are shown in Figure 15-2. More information on ERH applications at Navy sites can be found in the *NAVFAC Cost and Performance Review of ERH for Source Treatment* (NAVFAC, 2007).

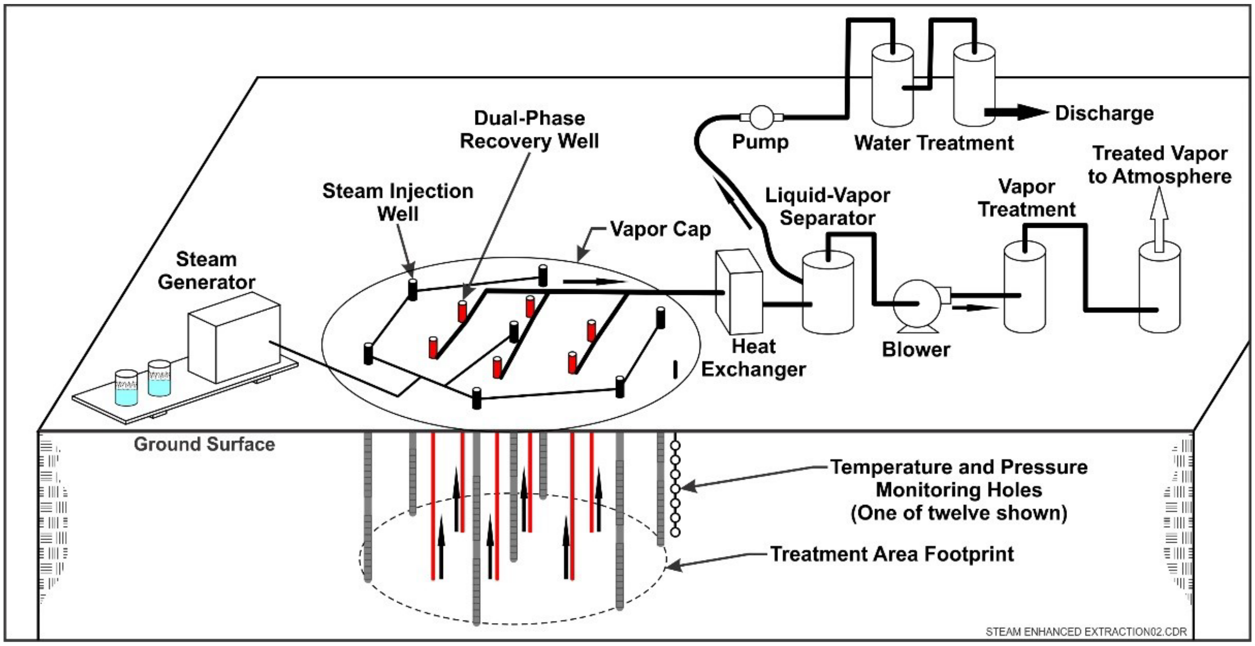


Figure 15-1. Steam Enhanced Extraction System (FRTR, 2020)

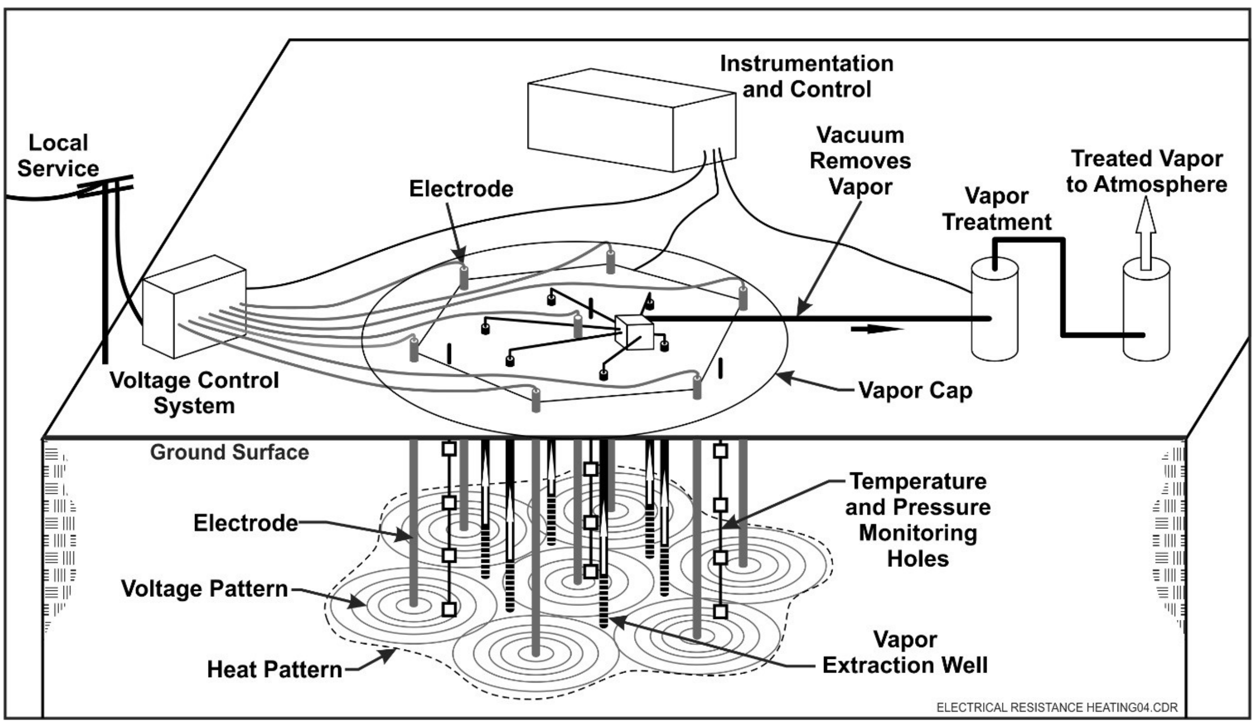


Figure 15-2. Electrical Resistance Heating System (FRTR, 2020)

Thermal Conductive Heating – TCH consists of heating the soil with an array of vertical heaters while simultaneously imposing a vacuum on the area. Heat flows from the 1200 to 1500°F heating elements through the soil primarily by thermal conduction or also through advection (via flowing groundwater or flowing steam). As the soil is heated, VOCs and SVOCs in the soil are vaporized and/or destroyed by a number of mechanisms, including: 1) evaporation into the subsurface air stream; 2) steam distillation; 3) boiling; 4) hydrolysis; 5) oxidation; and 6) pyrolysis. The vaporized water and contaminants are drawn into the vacuum extraction wells and treated in an above ground treatment system. The ground surface is covered by an insulating vapor barrier. If necessary, groundwater extraction may also be used to provide hydraulic control of the treatment area. The primary components of a typical TCH system are shown in Figure 15-3.

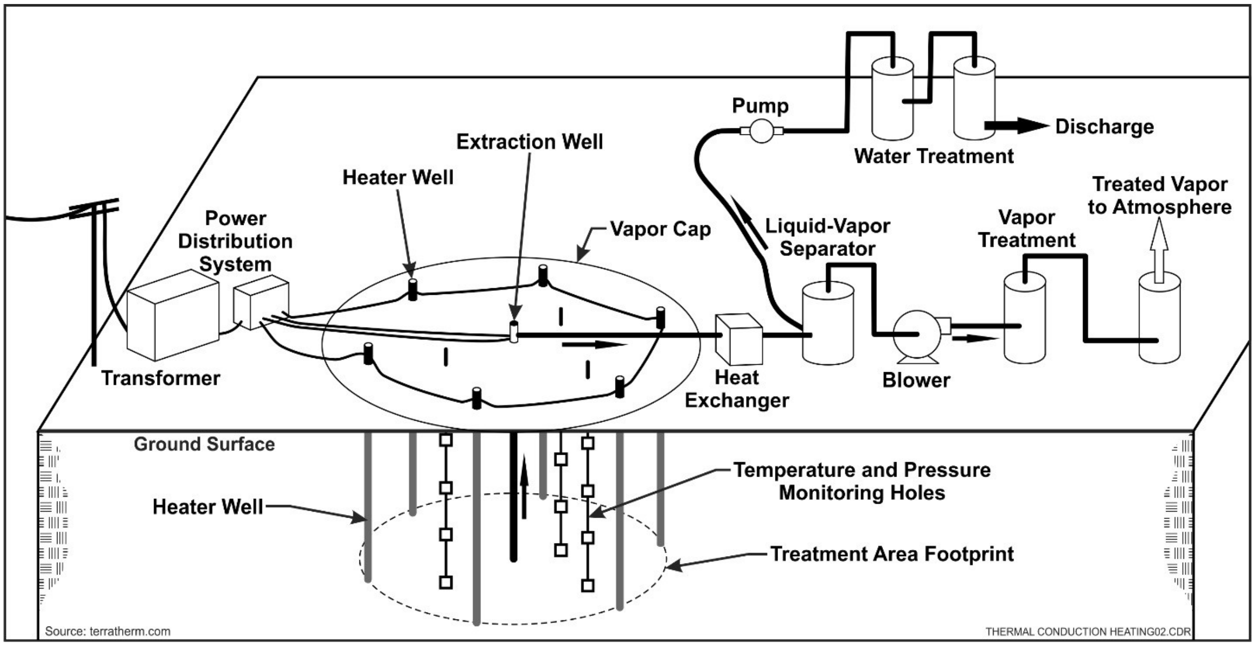


Figure 15-3. Thermal Conduction Heating System (FRTR, 2020)

15.2 Performance Plots

The effectiveness and efficiency of thermal treatment processes may be determined through performance plots. The data used to evaluate a thermal treatment system includes soil temperatures across the treatment area, duration required to reach desired temperature, contaminant concentrations, the volume of gas and vapor treated, and cost of system operations and maintenance. Performance plots of this data should be compared with remedial performance and cost objectives to determine the effectiveness and efficiency of the thermal treatment system.

A typical plot of cumulative mass recovered and concentrations of contaminants (VOCs in this case) versus time are shown in Figure 15-4. As shown in the figure, a typical contaminant concentration response curve for in-situ thermal treatment is characterized by initial high contaminant concentrations, followed by declining concentrations, and finally a period of in which concentrations reach asymptotic low levels. A plot of cumulative contaminant mass removal is a mirror image of the contaminant concentration response curve. Initially, the cumulative mass of contaminant removed increases rapidly. The initial response is followed by a period during which mass removal rates steadily decrease until, ultimately, asymptotic conditions are reached.

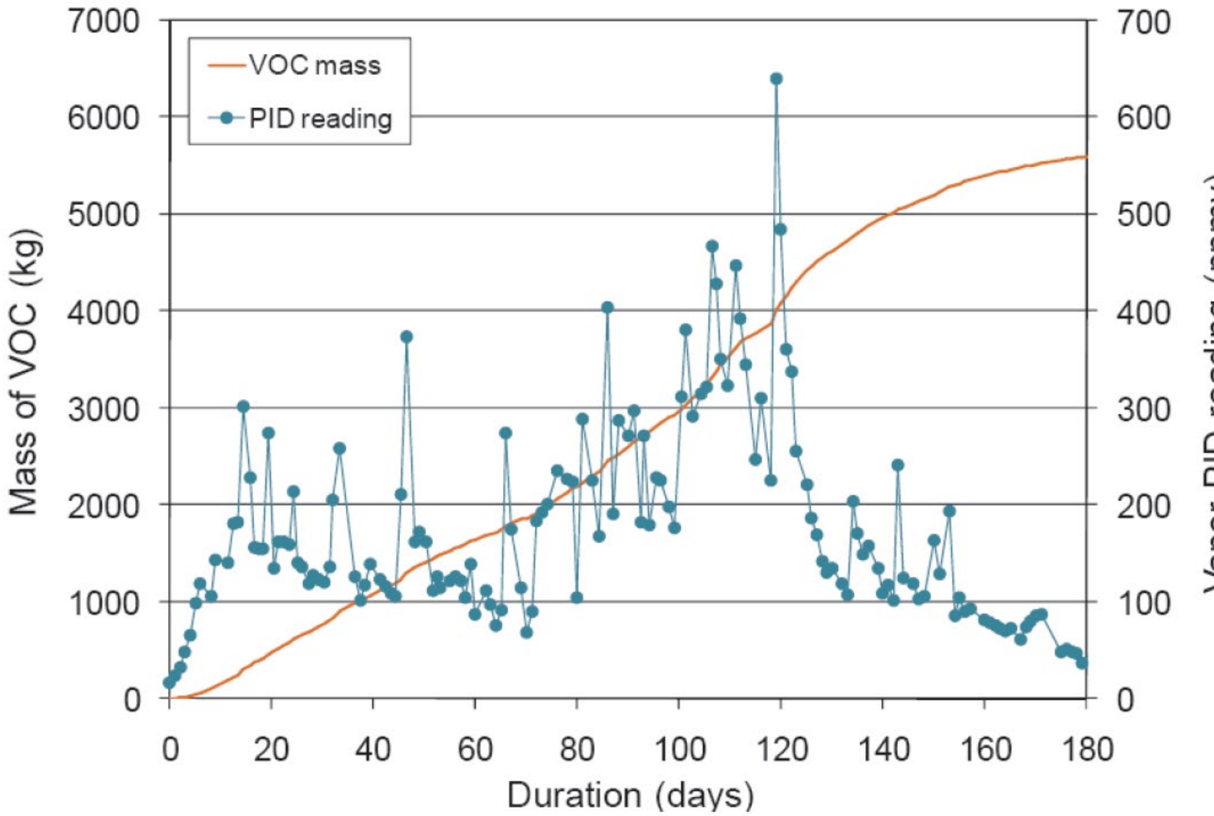


Figure 15-4. Mass Removal Using TCH at DoD Memphis Depot Facility, Tennessee (USEPA, 2014)

Example*: TCH was used to recover more than 12,000 pounds of CVOC contamination in a tight loess (silty/clay) above the water table at Dunn Field, located at the DoD Memphis Depot facility (Figure 15-4). Contamination was treated in eight distinct sub-zones comprising approximately 50,000 cubic yards out of a considerably larger total site footprint. In this case, investing time and resources in careful characterization to reduce the footprint requiring aggressive treatment by over 80 percent resulted in significant cost savings (USEPA, 2014).*

15.3 Common Operational Problems

Thermal treatment processes must be applied uniformly across the area of contamination. The existing site conditions must be evaluated to determine the appropriate use of these processes. The effectiveness of thermal treatment processes is primarily dependent of site conditions and treatment system design. ERH is most effective in treating sites with contamination in low permeability formations such as clay-rich portions of the vadose zone and aquifer, whereas steam injection is most effective in zones of moderate to high permeability. Higher permeability formations may not be evenly heated using ERH, and steam cannot penetrate the pore space as rapidly in low permeability soil, resulting in higher heat losses and the inability to completely heat the area. TCH can be effective in either high or low permeability formations, because thermal conductivity values vary over a very narrow range regardless of soil type. However, it is not well suited for sites with a high groundwater flow rate because the flowing groundwater works to cool the subsurface, reducing the conduction heating efficiency.

During implementation of ERH, heating vaporizes water from the subsurface, sometimes requiring a continual dripped supply of water to be added around each electrode to maintain adequate electrical conductivity (FRTR, 2020). In addition, the fraction of organic carbon (FOC) content can limit the effectiveness of any thermal treatment. Higher FOC content results in a slower release of contaminants from the subsurface, requiring longer treatment periods which make these energy-intensive treatment technologies less cost-effective. Operational problems resulting from improper treatment system design may result in the spread of contamination to clean areas. Common operational problems related to thermal treatment are provided in Table 15-1.

15.4 Common Optimization Recommendations

Optimization of operating problems resulting from site condition limitations will most likely require the use of an alternative technology. It is important to monitor temperature to ensure the soil is remaining at the desired temperature during the treatment duration. There are times when sections of the treatment area heats better than others. If this is the case, then the system can be optimized during treatment. Other design modifications may also be used to optimize thermal treatment systems.

Common optimization strategies for thermal treatment systems are provided in Table 15-1. These optimization recommendations provide a general approach as appropriate design modifications must be determined on a site-specific basis.

Table 15-1. Common Thermal Treatment Operational Problems and Optimization Strategies

Operational Problem	Potential Causes	Potential Negative Impacts on Performance	Optimization Strategy
Low contaminant removal rate.	• There is insufficient heating due to heating source inadequacies and/or site conditions (e.g., high soil moisture). • The fluid flow is not uniform. • The permeability of the soil is lower than estimated. • The injection wells or electrodes are not properly located. • There is interference from buried electrical conductors.	• Low temperatures will not allow contaminant removal. • The heat will be unevenly distributed. • The heat will be prevented from reaching the contaminants.	• Increase the size or capacity of the heat source. • Relocate and/or modify the injection wells, electrodes and/or recovery system. • Evaluate use of an alternate technology.
Undesired mobilization of the contaminants occurs.	• The injection/recovery system is not properly designed. • Utilities may provide a preferential flow pathway for mobilized contaminants to migrate outside of the treatment area.	• The contaminants may be spread to clean areas.	• Relocate and/or modify the injection wells, electrodes and/or recovery wells. • Install additional vapor recovery wells to contain vaporized contaminants of concern. • Do not perform heating near buried utilities.

16.0 AMENDMENT INJECTION

16.1 System Description

Many remedial technologies rely on injection of amendments or treatment media into the aquifer, including several discussed previously in this document such as ISCO, ISCR, EISB, PRBs, and in-situ adsorbents. A wide range of techniques can be applied to introduce and distribute amendments depending on the physical and chemical properties of the amendments and the characteristics of the area to be treated. A common challenge encountered during application of these technologies is the ability to achieve adequate distribution and contact between the amendments and contaminants of concern. Recent advancements in delivery methods provide novel ways to overcome the challenges encountered by conventional delivery methods, particularly to treat low-permeability formations or obstructed areas in the subsurface (FRTR, 2020; NAVFAC, 2020). Figures 16-1 and 16-2 show diagrams of two comment injection methods, direct injection and recirculation. These, along with other innovative injection methods, are described further below.

- **Direct injection** – Amendments are mixed with a specified volume of water and injected directly into the subsurface, displacing groundwater corresponding to the volume of amendment mixture injected. Because of this, there is a greater likelihood to displace contaminated groundwater from the treatment area compared to recirculation approaches. Direct push methods are well-suited for permeable materials because there tends to be sufficiently interconnected pore space to distribute the amendment throughout the treatment zone. In low permeability materials, such as silt and clay, the radius of influence may be limited and high pressure may develop, which can create preferential pathways through which amendments and groundwater may travel (FRTR, 2020).
- **Pneumatic and hydraulic fracturing** – Pneumatic fracturing is used to form fractures with controlled bursts of high-pressure gas, while hydraulic fracturing is performed by injecting a biodegradable slurry comprised of a viscosifier (e.g., guar gum) dissolved in water, which is polymerized using an additive to create a viscous gel. An enzyme is added to the gel to break it down shortly after injection. In order to keep the new fractures open, "proppants", which are solid granular materials (usually sand), can be used with both fracturing techniques. Fracturing is most applicable to low permeability formations, clay soils, glacial tills, bedrock, etc. in which the injection radius of influence is limited (FRTR, 2020).
- **Direct-push technology jet injection (DPT-JI)** – DPT-JI is an injection method that combines high-pressure jetting (10,000 pounds per square inch [psi]) and controlled hydraulic fracturing for emplacing amendments into low permeability matrices. The major benefit of DPT-JI resides in its ability to allow controlled delivery of amendments in fractures, which helps to avoid short-circuiting and to improve the contact of amendments with contaminants of concern. DPT-JI has a higher injection efficiency than conventional hydraulic fracturing and can deliver a greater quantity of amendment than DPT (NAVFAC, 2020).

- **Recirculation** – Groundwater is extracted from one or more extraction wells, amended with reagents and then reinjected into injection wells. Recirculation and mixing of amendments into groundwater is commonly performed using permanent injection and extraction wells, although a combination of direct push points and permanent wells can be used. Recirculation systems are designed to minimize displacement of contaminated groundwater compared to direct injection systems by creating flow pathways from the injection locations to the extraction locations, and for this reason recirculation is often selected for treatment of source areas to minimize displacement of contaminated groundwater to areas outside of the treatment zone (FRTR, 2020).
- **Horizontal wells** – Horizontal wells are a mature technology for a variety of remediation applications, but they have not been used widely for delivering in-situ amendments. The main advantage of horizontal wells is that the technology allows access to contamination located in obstructed subsurface areas (e.g., under a building or utility lines), which can be difficult to access with conventional vertical wells. Similar to fracturing, horizontal wells can be filled with reactive amendments to create a horizontal treatment zone at a target depth interval (NAVFAC, 2020).
- **Electrokinetics (EK)** – EK involves application of low voltage direct electrical currents in low-permeability geologic matrices to facilitate distribution of ionic and charged particle reactive amendments. The rate that dissolved ionic amendments move through the hydrogeological formation is driven by the electrical field and independent of the formation's permeability (NAVFAC, 2020). Most of the EK field applications to date are coupled with bioremediation (ESTCP ER-201325) or chemical oxidation (ESTCP-201626).

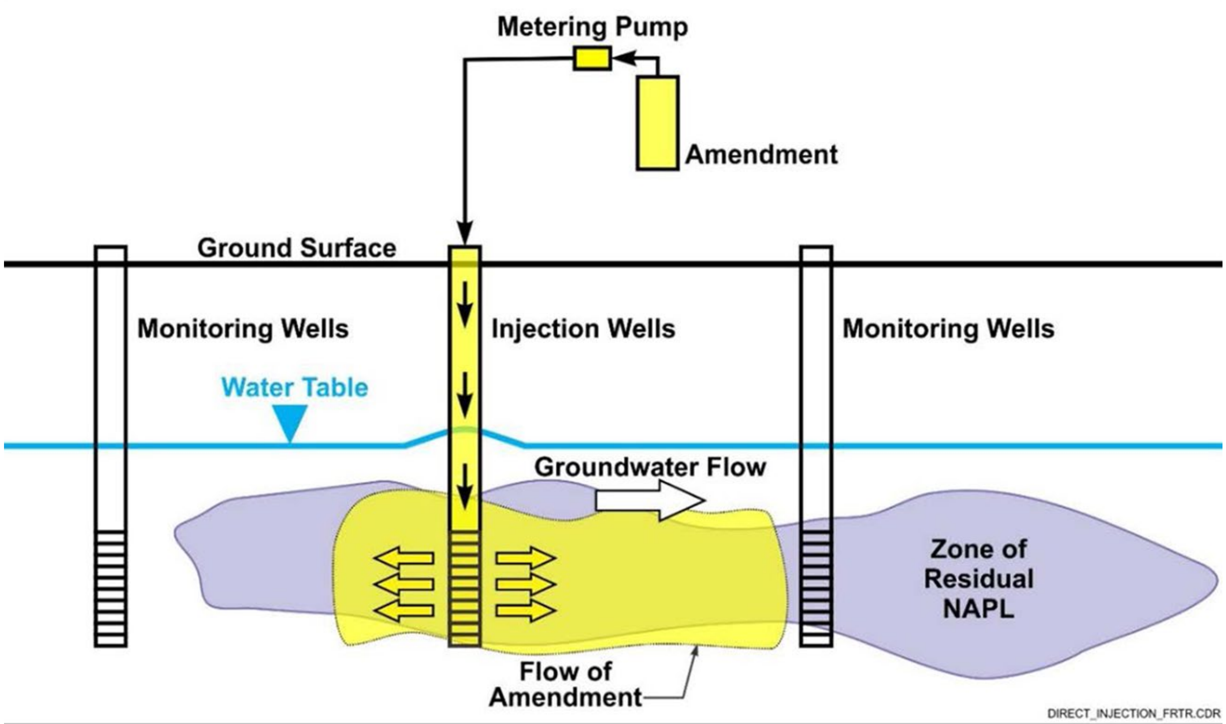


Figure 16-1. Direct Injection of Amendments (FRTR, 2020)

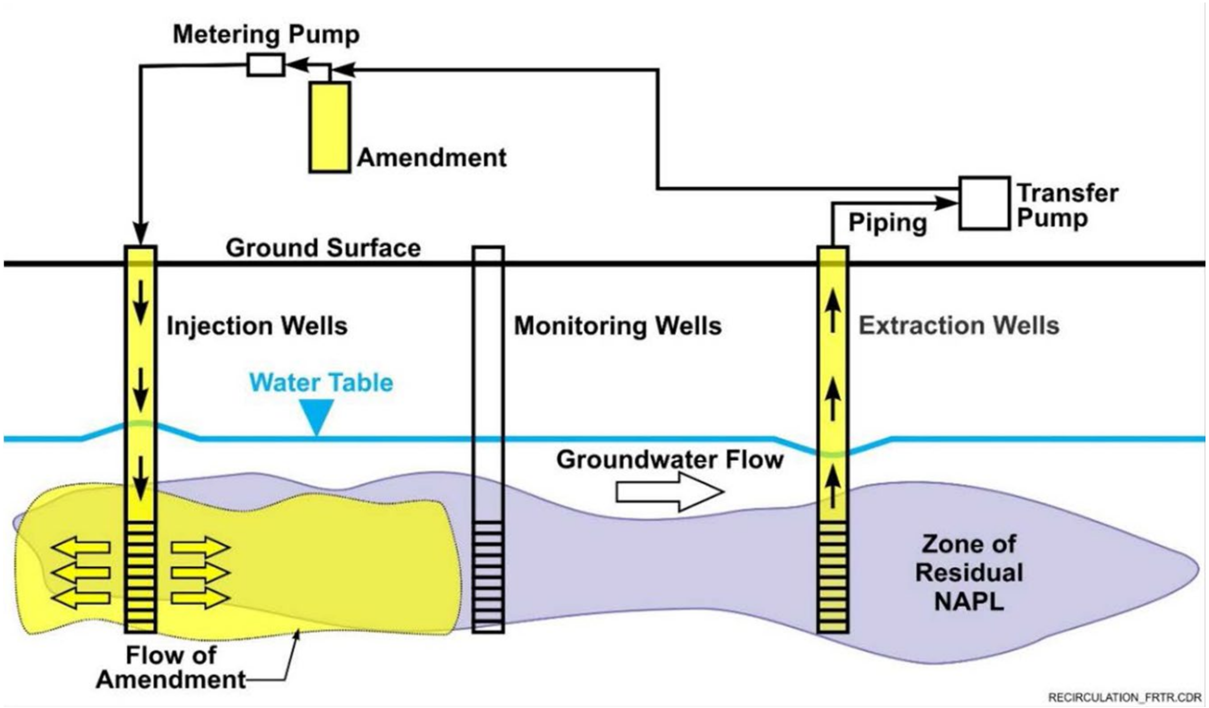


Figure 16-2. Groundwater Recirculation with Amendments (FRTR, 2020)

16.2 Performance Plots

Performance monitoring is an important component of an injection program to evaluate the effectiveness of amendment distribution. Performance monitoring of injection programs can include monitoring the injection process (injection pressure, flow rate, and volume) as well as real-time monitoring within the treatment zone (NAVFAC, 2013a). Geochemical parameters can be indirect indicators of an amendment injection, for example oxidants can increase oxidation reduction potential and possibly DO; persulfate increases conductivity; and electron donors and ZVI decrease oxidation reduction potential. With some amendments, visual observations such as color changes can also be used to monitor amendment distribution (e.g., purple color from permanganate injection, cloudy or milky white color from an emulsified oil injection, black color from activated carbon amendments). Field test kits (e.g., colorimetric kits) can be used to directly monitor some amendments, and also tracers, if used during an injection. Immediate results from real-time monitoring can be used to determine the radius of influence from the injection and to help optimize the injection program.

Figure 16-3 shows an example of a tracer breakthrough curve at a monitoring well located 20 ft downgradient of an amendment injection during a pilot study. The travel time for the center of bromide mass to reach the monitoring well was calculated to be 30 days and 18 days after the first and second injection, respectively. This indicated that the groundwater velocity was considerably higher than previously reported, and that more frequent injections would be needed at full scale than originally planned to maintain sufficient levels of amendments within the treatment area.

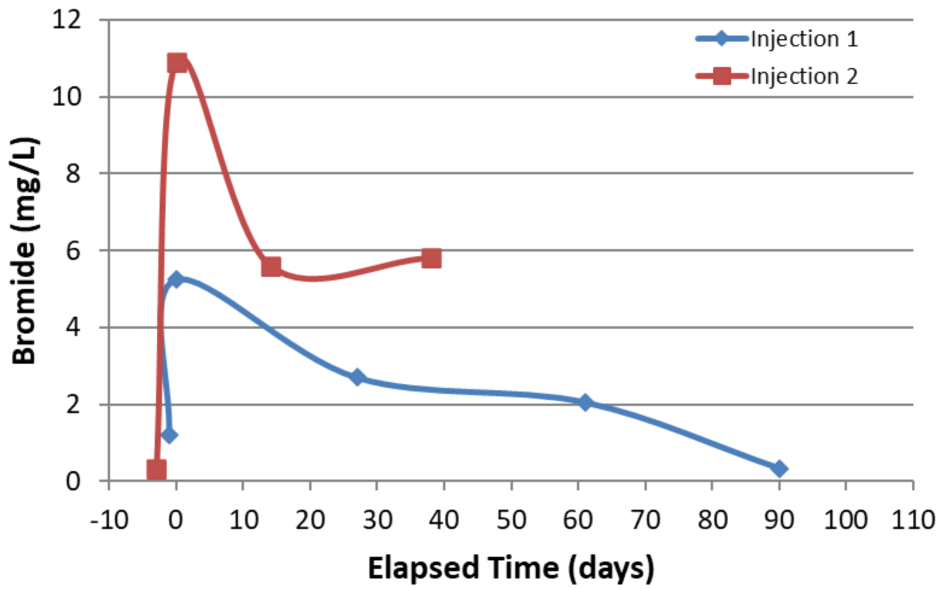


Figure 16-3. Bromide Tracer Breakthrough Curve

16.3 Common Operational Problems

Common operational problems may include issues such as higher or lower than expected injection pressures, lack of injection response at nearby monitoring wells, daylighting of amendments during injection, and observed injection responses outside of the target treatment zone (ITRC, 2020). An appropriately designed process monitoring program will identify these problems, and the monitoring data can be used to optimize the injection process. Common operational problems related to amendment injection are provided in Table 16-1.

16.4 Common Optimization Recommendations

Real-time process monitoring can be used to optimize the injection program both as it is implemented and for future injection events. Optimization considerations for amendment injection include injection point spacing, timing, quantities of amendments, and injection method employed (ITRC, 2020). For example, monitoring the radius of influence through indirect geochemical parameters can be used to optimize the injection point spacing for direct push injections and the volume of amendment injected. Data collected with respect to the injection process (e.g., injection pressure, flow rate) can be used to select an optimized injection method during future injections. Common optimization strategies for amendment injection are provided in Table 16-1.

Table 16-1. Common Amendment Injection Operational Problems and Optimization Strategies

Operational Problem	Potential Causes	Potential Negative Impacts on Performance	Optimization Strategy
Injection pressures are higher than expected.	• The formation permeability is lower than expected. • Biofouling or scaling may be blocking injection well screens.	• Unable to inject full volume of amendments. • Radius of influence is smaller than designed. • High pressures may result in unintended fracturing in subsurface or daylighting of amendments.	• Evaluate use of alternate injection method for low permeability zones. • Redevelop injection wells.
Injection pressures are lower than expected.	• Leaks in injection manifold or faulty pressure gauges. • Preferential pathways have been formed through repeated injections. • The formation permeability is higher than expected.	• Uneven distribution of amendments. • Injection impacts areas outside of the target treatment zone.	• Evaluate changes to the injection design or use of alternate injection method. • Ensure utility corridors are not located in proximity to the injection resulting in preferential pathways.
Lack of injection response at nearby monitoring wells.	• Preferential flow paths may be limiting effectiveness of the amendment injection. • Injection volume may be inadequate for optimal amendment distribution.	• Uneven distribution of amendments in the treatment zone. • Radius of influence is smaller than designed.	• Evaluate injection program design, including calculated amendment volume and loading to the treatment zone. • Evaluate use of alternate injection method.
Daylighting of amendments during injection.	• The formation permeability is lower than expected. • Injection pressures are too high for the formation.	• Uneven distribution of amendments in the treatment zone. • Radius of influence is smaller than designed.	• Evaluate changes to the injection design (lower injection pressures) or use of alternate injection method.
Injection response observed outside of the target treatment zone.	• The formation permeability is higher than expected. • Injection volume too great for target treatment zone.	• Contaminants may be mobilized to areas outside of the treatment zone.	• Evaluate changes to the injection design (lower injection pressures) or use of alternate injection method. • Evaluate injection program design, including calculated amendment volume and loading to the treatment zone.

17.0 MONITORED NATURAL ATTENUATION

Natural attenuation includes any of a number of biological, chemical, and physical processes that can effectively reduce contaminant toxicity, mobility, or volume to levels that are protective of human health and the environment. Some processes such as biodegradation and chemical transformation (abiotic degradation) destroy the contaminant mass. Other processes such as dispersion, dilution, sorption, and volatilization simply reduce the contaminant concentration.

Natural attenuation processes operate to some degree at all contaminated sites. However, the effectiveness of the processes in reducing contaminant mass or concentration depends on the type and amount of contaminants present and on the hydrogeology of the site. Natural attenuation is quite effective against petroleum constituents. Aerobic and anaerobic biodegradation are the two main attenuating mechanisms for petroleum constituents. Natural attenuation is also effective against chlorinated compounds under the proper site conditions. The primary attenuating mechanism of chlorinated compounds is anaerobic reductive dechlorination. Incomplete degradation can also produce breakdown products that are more toxic than the original compounds as in the case of VC production from tetrachloroethene/TCE degradation.

MNA is a cleanup remedy that combines reliance on natural attenuation processes with a program designed to monitor the progress of natural attenuation toward achieving cleanup objectives. The performance monitoring results are used to calculate the rate at which natural attenuation is occurring, which is compared to the rate predicted from site characterization data.

MNA has gained acceptance by regulatory agencies as a component in a comprehensive treatment train approach that incorporates engineered remediation systems. Treatment trains are selected as MNA can usually be implemented only after source control measures have eliminated the source of contamination. However, MNA has been implemented as a stand-alone remedy for some sites, particularly dilute plumes with no obvious contaminant source. MNA may require a contingency plan in the event that performance monitoring indicates that a cleanup objective (i.e., such as a pre-defined amount of plume spreading) is not being achieved within a reasonable time (to be determined by stakeholders based on site-specific conditions).

In certain situations, MNA can be an effective remedy and the most appropriate way to clean up a contaminated site. For example, sites contaminated with petroleum constituents are excellent candidates for MNA because petroleum constituents are among the compounds most easily destroyed through biodegradation. MNA may also be a good option at sites that have undergone some active remediation that has reduced contaminant source concentrations. In particular, MNA may be acceptable to regulators when active remediation systems have reached asymptotic conditions and are no longer effective or efficient at reducing contaminant concentrations. However, natural attenuation requires a longer time to achieve remedial objectives and typically requires more extensive site characterization and long-term monitoring than active remedial systems.

The following conditions are an initial indication that natural attenuation is occurring at a site:

- A contaminant plume that is stable or decreasing in size as documented by monitoring results.
- A consistent decreasing trend in contaminant concentrations (or mass flux/mass discharge) as documented by monitoring results.
- The presence of daughter products, other metabolic byproducts, and process-specific geochemical indicators.

If these conditions occur at a site, the RPM is encouraged evaluate natural attenuation occurrence and to study the feasibility of implementing MNA as a groundwater remedy.

MNA can be selected as a stand-alone remedy and/or implemented as a polishing step after a transition from an active remedy. A proposal to implement MNA must first include a demonstration that the natural attenuation processes will occur at a rate capable of reducing contaminants to acceptable concentrations before reaching a receptor. The demonstration is based on the CSM and supplemented by an evaluation of nutrients, electron donors, and electron acceptors and by information regarding natural attenuation rates. The data are incorporated into a model that predicts the time-of-travel and the distance and direction that contaminants will migrate prior to being degraded. Second, the proposal must include a plan for monitoring the progress of natural attenuation. The plan should identify a sufficient number of properly located wells for monitoring the constituents of concerns, biodegradation byproducts, and relevant geochemical parameters. The plan should specify the sampling frequency based on various site-specific factors, including proximity to receptors and constituent time-of-travel estimates. Third, the proposal may include a contingency plan in the event that performance monitoring indicates that natural attenuation is not occurring as predicted. The contingency plan would identify an alternative technology and specify the trigger criteria under which it would be implemented. For technology transitions, this contingency plan could include trigger criteria for temporary shutdown of an active remedy to evaluate if MNA is feasible.

Procedures for preparing a demonstration of MNA can be found in a number of readily available documents. These resources include the following:

- *Remedy Selection and Optimized Considerations for Monitored Natural Attenuation* (NAVFAC, 2021c),
- *Verification of Methods for Assessing the Sustainability of Monitored Natural Attenuation* (NAVFAC, 2013b),
- *Technical Guidelines for Evaluating Monitored Natural Attenuation at Naval and Marine Corps Facilities* (DON, 1998),
- *Technical Protocol for Implementing Intrinsic Remediation with Long-Term Monitoring for Natural Attenuation of Fuel Contamination Dissolved in Groundwater (*AFCEE, 1999),
- *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Groundwater* (USEPA, 1998), and

- *Estimating Cleanup Times Associated with Combining Source-Area Remediation with Monitored Natural Attenuation* (ESTCP, 2008).

While MNA is a passive remediation method, optimization steps can still be taken with respect to improving the monitoring approach. The CSM should be continually updated as data are collected as part of the MNA program. The monitoring plan should be reviewed on a regular basis and revised as needed to optimize the monitoring approach. MNA optimization may include monitoring fewer or different wells, reducing the frequency of monitoring as trends are established over time, and revising the parameters included in the monitoring plan. Optimization strategies for MNA are provided in Table 17-1.

Available resources to optimize the monitoring approach for MNA include the following:

- *Remedy Selection and Optimized Considerations for Monitored Natural Attenuation* (NAVFAC, 2021c),
- *The Importance of Abiotic Transformations in Natural Attenuation of Contaminated Groundwater* (NAVFAC, 2022),
- *Environmental Molecular Diagnostics: Molecular Biology-Based Tools* (NAVFAC, 2021d), and
- *Environmental Molecular Diagnostics: Chemical-Based Tools* (NAVFAC, 2021e).

Table 17-1. Common Monitored Natural Attenuation Optimization Strategies

MNA Challenge	Potential Causes	Potential Negative Impacts on Performance	Optimization Strategy
Trend analyses of MNA data are difficult to interpret.	• Sampling variability between monitoring events affects monitoring data. • Seasonal fluctuations impact monitoring data results.	• Trend analyses are difficult to interpret. • Plume stability evaluations are questioned.	• Collect sufficient data to establish statistically significant trends.
Redox conditions appear unfavorable for naturally occurring biodegradation.	• Dissolved oxygen measurements may be unreliable. • Available monitoring data does not adequately characterize redox conditions at the site.	• Limited data set leads to misinformed conclusions regarding redox conditions and COC degradation pathways.	• Monitor dissolved iron, sulfate and methane in addition to dissolved oxygen to better evaluate redox conditions. • Apply line of evidence approach to also include MBTs and iron-bearing minerals to fully evaluate all biological and abiotic degradation pathways.
Monitoring data suggest that cleanup goals may not be achieved within an acceptable timeframe.	• CSM is not well-developed. • Degradation mechanisms acting at the site are misunderstood.	• Predictive fate and transport models may be unreliable. • Incomplete CSM leads to misinformed conclusions regarding effectiveness of MNA.	• Collect additional data to fully develop the CSM, including site-specific geology. • Collect additional data to better characterize the degradation mechanisms (biological or abiotic) and rates.
Long-term monitoring associated with MNA remains costly due to the extensive list of monitoring requirements.	• CSM has not been updated to inform optimization of the monitoring program.	• Unnecessary data continues to be collected despite changes to the CSM over time. • Costs are incurred to collect data that is no longer relevant or required to meet the monitoring goals.	• Update the CSM and eliminate monitoring points from the program if they are no longer strategically located relative to the current plume configuration. • Reduce monitoring frequency if long-term trends have been established based on a statistically significant dataset. • Eliminate sampling parameters if the data is no longer needed to demonstrate MNA.

18.0 ABOVE GROUND TREATMENT SYSTEMS

Many liquid phase and vapor phase treatment technologies are available for use with remedial systems. An effluent treatment system can be a combination of many treatment components depending on the characteristics of the contamination. The best way to optimize the operational cost involved with using effluent treatment technologies is to:

- Avoid overly complex processes;
- Apply the technology properly;
- Identify unnecessary or inefficient treatment steps or equipment;
- Modify/change systems as contaminant characteristics/concentrations change;
- Look for economical pretreatment processes to reduce maintenance;
- Increase automation to reduce labor costs an increase treatment reliability; and
- Size equipment properly for maximum efficiency and optimal energy usage.

This section provides an overview of effluent treatment technologies and general guidelines for reducing operational costs of effluent treatment systems. Additional information about optimization of above ground treatment systems is provided in the ITRC document titled *Above Ground Treatment Technologies* (ITRC, 2006).

18.1 Vapor Phase Treatment Technologies

The most common remedial technologies that generate contaminated vapors are SVE systems, MPE systems, thermal treatment systems, and water treatment systems using air strippers. The appropriate regulatory agency should be consulted to determine the control level required for the system. Vapor phase treatment technologies discussed in this section include thermal oxidation, catalytic oxidation, and GAC. A brief summary of each technology is provided below.

The range of anticipated soil vapor concentrations that will be encountered throughout the project should be considered when selecting a vapor treatment system. Sequential implementation of more than one treatment system (e.g., catalytic oxidation while high removal rates are occurring followed by activated carbon when the concentrations decrease) may be necessary. Table 18-1 lists the concentration ranges where the technologies are applicable.

Table 18-1. Applicability of Vapor Treatment Technologies

Technology	Influent Concentration (ppmv)
Thermal oxidation	1,000 to 5,000
Catalytic oxidation	100 to 3,000
Granular activated carbon	1 to 300

Table 18-2 identifies optimization guidance for vapor treatment technologies. This guidance can be used to remedy common problems encountered with these technologies.

Table 18-2. Vapor Treatment System Optimization Guide

Condition Requiring Optimization	Probable Cause	Potential Impacts to Performance	Potential Actions to Optimize Performance
Thermal Oxidation System			
Operating costs are rapidly increasing.	• Incoming vapor concentration dropping • Incoming vapor composition changing	• Increase in supplemental fuel use	• Consider other less expensive treatment technologies.
Air emissions constituents are rapidly increasing.	• Incorrect operating temperature • Incorrect fuel/vapor/dilution air ratios	• Decrease in destruction removal efficiency	• Reset operating temperature. • Reset fuel, vapor, and dilution feed valves.
System components experience "burn through."	• Excessive combustion temperature • Refractory brick damage • Insulation damaged	• System shutdown	• Check thermocouple and fuel inlet and influent valves for proper operation. • Replace refractory brick. • Replace insulation.
Catalytic Oxidation Systems			
Air emissions constituents are rapidly increasing.	• Incorrect operating temperature • Incorrect fuel/vapor/dilution air ratios	• Decrease in destruction removal efficiency causes exceedance of emission limits	• Reset operating temperature. • Reset fuel, vapor, and dilution feed valves.
System components experience "burn through."	• Excessive combustion temperature	• System shutdown	• Check thermocouple and fuel inlet and influent valves for proper operation.
Destruction efficiency decreases over time.	• The catalyst becomes degraded, poisoned or eroded due to either high temperatures or contaminants that are not compatible with the catalyst.	• Decrease in destruction removal efficiency causes exceedance of emission limits	• Check thermocouple and fuel inlet and influent valves for proper operation. • Determine and eliminate the source of the poisoning contaminant. • Change out the catalyst. • Change to alternate technology.
Activated Carbon Adsorption			
Frequent carbon bed replacement.	• Incorrect inlet temperature • High relative humidity • Incorrect sizing of bed	• Substantially less adsorption performance • Operational time decreased	• Incoming vapor stream temperature between 80 and 100°F. • Condition vapor stream through heat exchangers. • Properly size the unit for flow and mass that is to be treated.
Low flow through the carbon bed.	• Biological growth on carbon • High particulate loading	• Reduced adsorption performance • Frequent changeout of containers	• Pre-treatment of vapor stream prior to carbon adsorption treatment.
55-gallon containers develop leaks.	• Influent chemistry incompatible with container materials	• Frequent changeout of containers prior to reaching carbon capacity	• Choose a container that is constructed of material that is compatible with effluent being discharged and treated.
55-gallon containers develop bulges on top/bottom.	• Incorrect pressure of incoming waste stream	• Frequent changeout of containers/leaking containers	• Install valving to control the pressure of the incoming effluent stream.

Thermal Oxidation – Thermal oxidation is accomplished by direct heating of contaminated vapor stream at elevated temperatures (1,200 to 1,600°F) with resultant production of combustion gases, such as carbon dioxide and water vapor. Thermal oxidation units typically are used to treat halogenated and nonhalogenated VOCs and SVOCs, and polychlorinated biphenyls (PCBs). This technology is often utilized during the initial phase of site remediation when contaminant concentrations are high. As concentrations drop, power and fuel consumption generally rises dramatically.

Catalytic Oxidation – Catalytic oxidation thermally oxidizes the contaminated vapor stream by passing the vapor over an inert catalyst bed, which promotes the oxidative destruction of the contaminants to combustion gases. The catalyst allows the reaction to occur at much lower temperatures (600 to 1000°F) than during normal combustion processes, which decreases need for supplemental fuel. Because of the catalyst costs, catalytic oxidizers usually will have a higher capital cost than a thermal oxidizer, although the operating costs are usually lower.

As with thermal oxidation, catalytic oxidation can be used to treat halogenated and non-halogenated VOCs and SVOCs, and PCBs. A key consideration for catalytic oxidation systems, however, is the potential for catalyst poisoning or erosion. Materials such as halogens, heavy metals, or solvents can poison or mask the catalyst material, thus requiring either periodic cleaning or premature replacement of the catalyst bed. Vapor streams containing high particulate levels can have a similar effect by eroding the catalyst material.

Granular Activated Carbon – GAC treatment is performed by passing a contaminated vapor stream through one or more vessels containing activated carbon, which removes contaminants from the vapor by adsorption. GAC is used because its high surface area allows for significant adsorption over a wide range of concentrations and chemicals. The amount of adsorption is determined by the chemical, temperature, and pressure at which the adsorption takes place. GAC is used to treat halogenated and non-halogenated VOC and SVOC and PCBs; GAC has limited adsorption capacity for ketones and generally poor adsorption of volatile alcohols.

18.2 Liquid Phase Treatment Technology

An extracted water treatment system can be a combination of many treatment components, depending on the characteristics of the contamination. The most effective treatment technology during the early stages of the remedial action may not be the most cost-effective during latter stages. In fact, the question of whether any treatment is needed should be periodically examined as the remediation progresses. Liquid phase treatment technologies discussed in this section include air stripping, GAC, ultraviolet oxidation, and metals precipitation. A brief summary of each technology is provided below.

Table 18-3 identifies the optimization guidance for liquid treatment technologies. Optimization of pretreatment methods commonly associated with these treatment technologies is also included. This guidance can be used to remedy common problems encountered with these technologies.

Air Stripping – Air stripping is used to separate contaminants from groundwater by increasing the surface area of the contaminated water and exposing it to air. Types of aeration methods include

Table 18-3. Liquid Treatment System Optimization Guide

Condition Requiring Optimization	Probable Cause	Potential Impacts to Performance	Potential Actions to Optimize Performance
Pre-treatment Systems			
Free-phase oil is entering groundwater treatment system	• Oil/water separator is not functioning correctly • Clay/anthracite filter vessel is clogged	• Reduced treatment efficiency of treatment system	• Clean oil/water separator. • Adjust the skimming or coalescing plates in the oil/water separator. • Replace the clay/anthracite filter vessel.
Suspended solids are entering treatment system components	• Filters are clogged, torn, or undersized.	• Creates backpressure on treatment equipment or clog treatment equipment, which will make the treatment less efficient.	• Resize bag filters to accept a higher flow. • Replace the bag filter with a new one. • Consider placing the bag filters in series for greater efficiency. Use large pore size on the first filter with decreasing pore size on subsequent filter(s).
Suspended solids are being "created" in the treatment system and clogging system components	• Oxidation of metals (iron or manganese) • Scaling due to carbonates	• Premature plugging or coating of tubing, piping, vessel walls, packing materials, filters, and carbon	• Use a water softener or adjust the pH • Chelate metals using an oxidation tank • Use a sequestering agent
Air Stripping System			
Flooding of stripping tower	• Tower packing is clogged	• Loss of treatment efficiency due to short circuiting or clogging	• Clean tower packing and install pretreatment equipment (filters or oxidation tanks) • Use sequestering agent • Check influent flow rate into tower
Effluent concentration from tower suddenly or slowly rises over time	• Tower packing is clogged. • Air blower is not functioning correctly or duct is leaking.	• Loss of treatment efficiency	• Clean tower packing and install pretreatment equipment. • Adjust air/water ratio to correspond to the design concentrations of contaminants for the removal efficiency.
Activated Carbon Adsorption			
Effluent flow and pressure drops suddenly	• Carbon media is clogged.	• Loss of treatment efficiency	• Replace carbon media. • Install pretreatment filters prior to carbon media.
Pressure vessels leak or bulge	• Carbon vessel designed for low flows	• Shutdown of treatment system	• Replace with fiberglass vessels that are designed for higher flow rates.
Significant increase in effluent concentrations	• Carbon media is spent.	• Loss of treatment efficiency	• Replace spent carbon. • Install pre-treatment units prior to carbon vessels.
Ultraviolet (UV)/Oxidation			
Significant increase in effluent concentrations	• High turbidity causes interference • Fouling of quartz sleeves • High concentrations of chemical additives	• Loss of treatment efficiency	• Install pre-treatment units prior to UV/oxidation system. • Adjust chemical additive concentrations.

Table 18-3 (continued). Liquid Treatment System Optimization Guide

Condition Requiring Optimization	Probable Cause	Potential Impacts to Performance	Potential Actions to Optimize Performance
Metal Precipitation			
Increase in total residual metals concentration	• Presence of organic and inorganic species (other than hydroxide) resulting in the formation of soluble species with metal ions increasing total residual metals concentration (particularly cyanide, ammonia, EDTA, and carbonate) • Process stream temperature variations • Insufficient detention times (i.e., rapid mix, floc, settling, filtration) • Improper coagulant dosing • Presence of multiple metal species • Improper pH adjustment • Improper rapid mix and flocculation mixing rates	• Decrease in treatment efficiency • Deviations between calculated and observed values of metal removal	• Conduct periodic jar tests to determine optimal chemical selection and dosing, and optimal overflow rates. • Modify rapid mix and flocculation mixing rates based on jar test data.
Increase in quantity and moisture content of sludge	• Improper reagent (i.e., coagulant, flocculant, caustic, acid) dosing • Improper mixing rates	• Increase in sludge handling costs	• Conduct periodic jar tests to ensure optimal chemical selection and dosing. • Modify rapid mix and flocculation mixing rates based on jar test data.
Decrease in settling and filtration efficiencies	• Excess sludge accumulation in filtration and settling units	• Decrease in treatment efficiency	• Perform O&M on settling and filtration unit (e.g., remove sludge).

packed towers, diffused aeration, tray aeration, and spray aeration. Air stripping is used to remove halogenated and non-halogenated volatile organic compounds and is less effective for contaminants with low vapor pressure of high solubility.

Granular Activated Carbon – Liquid-phase GAC treatment is performed by pumping groundwater through one or more vessels containing activated carbon, which removes contaminants from the water stream by adsorption. Liquid-phase GAC is especially effective for polar compounds and can be used to treat halogenated and nonhalogenated VOCs, SVOCs, PCBs, and PFAS. Carbon adsorption is effective for removing contaminants at low concentrations (less than 1 mg/L) from water at nearly any flowrate, and for removing higher concentrations of contaminants from water at low flowrates.

Advanced Oxidation Process (AOP) – AOP refers to a set of chemical treatment processes used for treatment of organic chemicals in wastewater (e.g., MTBE, 1,4-dioxane, VOCs, SVOCs, PCBs, pesticides, ordnance compounds) through the production of active hydroxyl radical that breaks down contaminants to carbon dioxide, water and salts. Examples include ultraviolet (UV)/peroxide, titanium dioxide/UV, and ozone/peroxide (HiPOx). Systems which use UV light also provide chemical destruction by photochemical oxidation of the organic contaminants.

Metals Precipitation – Metals precipitation involves adding a chemical precipitant to extracted groundwater to remove inorganic contaminants. The dissolved metals are converted to an insoluble form by a chemical reaction between the soluble metal compounds and the precipitant. The resultant suspended solids are separated out by settling in a clarifier. Chemical precipitants include calcium hydroxide (lime), sodium hydroxide, ferrous sulfide, sodium sulfide, sodium hydrosulfide, sodium carbonate, calcium carbonate, and sodium borohydride. Target contaminant groups are heavy metals.

18.3 Discharge and Disposal Options

Treated water disposal/discharge alternatives can include:

- Discharge to local publicly owned treatment works (POTW),
- Discharge to surface water,
- Reinjection, and
- Other (i.e., irrigation, industrial reuse such as dust control, or use as washwater).

The implementation of these options is highly site-specific and should be evaluated on a site-specific basis.

18.4 Remedial System Decommissioning

After decommissioning, the entire remedial system or its components may be reused or salvaged. Ideally, the entire remedial system or its components would be reused at another remedial site on the given installation, used for another purpose at the installation, or used at another DoD site or installation. A less desirable option is to sell components for salvage value.

Equipment Reuse – RPMs should consider the applicability of existing equipment to their site. The transfer of remediation equipment between sites would result in significant cost savings, as well as provide other benefits. The following steps should be conducted to determine whether a particular remedial system can be reused:

- Maintain an Accurate Remedial System Inventory. The inventory should include pertinent details of process equipment, such as discharge pump sizes, blower sizes, treatment system type, maximum and minimum system throughput, and instrumentation provided with the system. This information will allow RPMs at other installations to determine whether a particular system will meet the needs of their particular site.
- Maintain a Current Site Closeout Schedule. If a remedial system is determined to be suitable for use at another site or installation, the remedial system must be available for use at the required time. Knowing when a suitable system is available for reuse can allow RPMs to proactively negotiate a schedule extension if reuse of a system can save significant funding.
- Inform Other Parties of Equipment Availability and Schedule. Other parties should be informed of equipment inventory and availability. Facilities and engineering support groups may identify a need for the remedial system or system components.

Equipment Salvage – If equipment reuse options are not identified, equipment salvage should be pursued. The Defense Reutilization and Marketing Office (DRMO) is usually the appropriate agency to coordinate equipment resale. The DRMO temporarily stores excess materials before reutilization or public sale. Because DRMOs are permitted hazardous materials/waste treatment, storage, and disposal facilities, they could appropriately handle any contaminated equipment and possibly determine appropriate reuse or disposal options.

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