



**New Jersey  
Department of Environmental Protection**



**Site Remediation and  
Waste Management Program**

**In Situ Remediation:  
Design Considerations and Performance  
Monitoring Technical Guidance Document**

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# 1. INTENDED USE OF TECHNICAL GUIDANCE

This technical guidance is designed to help the person responsible for conducting the remediation to comply with the Department requirements established by the Technical Requirements for Site Remediation (Technical Rules), New Jersey Administrative Code (N.J.A.C.) 7:26E. Many different people involved in the remediation of a contaminated site will use this technical guidance, such as licensed site remediation professionals (LSRP), non-LSRP environmental consultants and other environmental professionals. Therefore, the generic term “investigator” will be used to refer to any person that uses this technical guidance to remediate a contaminated site on behalf of the person responsible for conducting the remediation. This technical guidance does not provide information on the selection of a remedial action, but rather is intended to provide information on performance monitoring of a selected remedy. The inclusion of specific reference documents within this technical guidance is not intended to modify or otherwise alter compliance with N.J.A.C. 7:26E.

The procedures for a person to vary from the technical requirements in regulation are outlined in the Technical Rules at N.J.A.C. 7:26E-1.7. Variances from a technical requirement or departure from technical guidance must be documented and adequately supported with data or other information. In applying technical guidance, the Department recognizes that professional judgment may result in a range of interpretations on the application of the technical guidance to site conditions. The requirement for the person responsible for conducting the remediation to apply Department technical guidance as appropriate is at N.J.A.C. 7:26C-1.2(a)3 of the Administrative Requirements for the Remediation of Contaminated Sites (ARRCS).

This technical guidance supersedes previous Department guidance issued on this topic. Technical guidance may be used immediately upon issuance. However, the Department recognizes the challenge of using newly issued technical guidance when a remediation affected by the technical guidance may have already been conducted or is currently in progress. To provide for the reasonable implementation of new technical guidance, the Department will allow a 6-month “phase-in” period between the date the technical guidance is issued final (or the revision date) and the time it should be used.

This technical guidance was prepared with stakeholder input. The following people were on the committee who prepared this document:

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## **2. PURPOSE**

This technical guidance document details site characterization concerns, selected design considerations and the performance monitoring associated with in situ remedial actions used for treating both contaminated ground water and soil. This document is meant to enhance the guidance on these topics found in the Ground Water Technical Guidance: Site Investigation, Remedial Investigation, Remedial Action Performance Monitoring (Ground Water Technical Guidance) in conjunction with other related technical guidance, which can be found in SRP Guidance Library (<http://www.nj.gov/dep/srp/guidance/>).

Additionally, this document provides guidance to the investigator on crafting discharge to ground water (DGW) proposals to expedite the Department's review of them and issuance of approval letters required by the New Jersey Pollutant Discharge Elimination System (NJPDES) Permit-by-Rule (PBR) in N.J.A.C. 7:14A-7.5(b). This document also attempts to raise awareness of other potential considerations (e.g., other permits, health and safety issues) that may be encountered during implementation of an in situ remedy (treatment in place). It should be used in conjunction with the most updated version of the following additional permit or administrative guidance: NJPDES Discharges to Ground Water Technical Manual for the Site Remediation Program (NJPDES DGW technical manual); Remedial Action Permits for Ground Water (RAP-GW); Remedial Action Permits for Soil (RAP-Soil) and the ground water Classification Exception Area (CEA) guidance and related form instructions.

## **3. INTRODUCTION**

This document provides site characterization and remedial action design information that the investigator should consider when designing and implementing in situ remedial action technologies and it provides guidance for developing a performance monitoring program. A performance monitoring program should be used to demonstrate the effectiveness of in situ

remedial action technologies in terms of achieving the applicable remediation standards, interim goals or remediation objectives (e.g., source reduction/elimination). In accordance with N.J.A.C. 7:26E-5.1, 5.2, and 5.6, the performance monitoring program shall also demonstrate that the remedy itself and any associated discharge:

- mitigates or prevents receptor exposure
- does not cause unpermitted or uncontrolled negative impacts or a natural resource injury
- protects human health, safety and the environment
- complies with all other applicable federal, state and local laws and regulations, including the NJPDES PBR requirements for a DGW proposal

As explained in more detail in Section 5.1 below, performance monitoring for in situ remedial actions involves the collection and evaluation of data both during and following treatment, and the comparison of that information to pretreatment or baseline conditions and to the applicable regulatory standards. Performance monitoring is required to assess the effectiveness and protectiveness of in situ remedial technologies that remove, treat, or isolate contaminants within the vadose and saturated zones. The following general types of processes are associated with these technologies and Section 6 of this guidance is organized based on these three categories:

- **Biological Processes** – In situ technologies utilizing aerobic processes include those where oxygen or atmospheric air are directly or indirectly introduced into soil or ground water to stimulate or enhance aerobic microbial degradation of contaminants. Technologies applying anaerobic biological processes use various forms of electron donor substrates usually designed to stimulate growth of microorganisms that carry out degradation of organic compounds. The addition of nutrient supplements, enzymes or microbial cultures to the subsurface can be part of both aerobic and anaerobic bioremediation technologies.
- **Physical and Chemical Processes** – A wide range of in situ remedial action technologies use and combine physical and chemical processes such as solidification, stabilization, soil flushing, surfactant injection, soil vapor extraction, hydraulic containment, air or oxygen sparging, and chemical oxidation and reduction.
- **Thermal Processes** – Technologies such as electrical resistance heating, steam enhanced extraction, and thermal conduction heating use heat to mobilize contaminants to enable and enhance their recovery from the subsurface and in some cases, destroy them in situ. In situ vitrification applies electricity, via insertion of electrodes into the subsurface, to melt contaminated soils so they become a solid mass of glass-like material, thereby trapping or destroying contaminants. The heat from any of these technologies may also enhance the biological, physical, and chemical processes that are part of in situ remediation.

The Contaminated Site Clean-Up Information (CLU-IN) Web Site provides useful information about many in situ remedial action technologies used at Superfund and other contaminated sites.

For general information on remedial action technologies presented in layperson's terms visit a *Citizen's Guide to Cleanup Technologies* at <http://www.clu-in.org/products/citguide/>. For more technical information regarding remedial technologies visit CLU-IN's *Remediation Technology* page at <https://clu-in.org/remediation/> or visit Environmental Restoration (ER) Wiki at [http://www.environmentalrestoration.wiki/index.php?title=Main\\_Page](http://www.environmentalrestoration.wiki/index.php?title=Main_Page).

### **3.1. DOCUMENT OVERVIEW**

Subsections 3.2 and 3.3 below explain the regulatory basis and the general health and safety requirements that apply to implementing and monitoring in situ remedial actions. The remaining sections 4 through 8 of this guidance are titled as follows:

- Site Characterization and Remedial Design
- General Performance Monitoring Objectives
- Technology Specific Performance Monitoring
- Permitting
- Reporting

The investigator should apply the site characterization and remedial design information in Section 4 when designing and implementing the remedial action, when developing monitoring objectives and in designing a monitoring program capable of documenting when the various objectives have been obtained.

The investigator should apply the general guidance in Section 5 and the technology specific guidance in Section 6 when preparing both the monitoring plan in a remedial action work plan (RAW) and the monitoring plan in a DGW proposal. These sections should also be used, as applicable, when developing monitoring and evaluation plans for a Remedial Action Permit (RAP) application for active ground water remediation required per N.J.A.C. 7:26C-7.5(d)5 and 6 of ARRCs. This guidance was written with the expectation that at most sites the in situ remedial technologies discussed in this guidance will be completed before a RAP-GW application is submitted.

Section 7.1 provides specific guidance regarding the DGW proposal and the NJPDES PBR used by Site Remediation Waste Management Program (SRWMP) to allow discharges that are part of implementing an in situ remedial action technology. Section 7.1 covers PBR reporting and compliance issues and Section 7.2 briefly discusses other types of permits or approvals that the investigator may need to implement an in situ remedial action. Section 7.3 addresses the RAP-GW. After a remedial action report (RAR) is submitted and the remedial action implemented includes a CEA, a ground water RAP regulates the long term operation, maintenance and monitoring of the remedial action.

Section 8 provides guidance on reporting requirements associated with all key documents but predominantly the RAW and RAR.

### **3.2. REGULATORY BASIS**

Technical Rule requirements for performance monitoring of remedial actions are at N.J.A.C. 7:26E-5.1(a), (d)1 through 6 and (e); 5.2(a)1 through 3; 5.5(b) and (c), and 5.6. ARRCs requirements for monitoring active remedial actions are at N.J.A.C. 7:26C-7.5(d).

**N.J.A.C. 7:26E-5.1 and 5.2** requirements apply to all aspects of an in situ remedy including any pilot test/design study and proposed DGW, which are part of developing or implementing a remedial action. The definition of remedial action is at N.J.A.C. 7:26E-1.8. The PBR provision of N.J.A.C. 7:14A-7.5(b) 1, and operating requirements for Class V injection wells at N.J.A.C. 7:14A-8.16(c), establish that compliance with the pertinent requirements of N.J.A.C. 7:26E-5.1 and 5.2 is a condition of obtaining and continuing to have a permit-by-rule.

**N.J.A.C. 7:26E-5.5** covers the RAW which, per N.J.A.C. 7:26E-5.2(a)2 and 5.5(b)6, must include a monitoring program or plan and also, per Section 5.5(b)4, the results of any pilot test, bench scale or design study. Per N.J.A.C. 7:26E-5.1(d)4 and (d)5 and 5.2(a)3, the person developing the RAW monitoring plan must use the resulting data, where applicable, to demonstrate remediation to the numeric and narrative Remediation Standards, N.J.A.C. 7:26D, and, if applicable, compliance with any other Federal, State and local requirements.

**N.J.A.C. 7:26D** includes numeric ground water, surface water and soil remediation standards. Narrative remediation standards are also included for ground water and surface water. Although the emphasis in this document is on ground water monitoring, monitoring of other media may also be needed to demonstrate compliance with some applicable narrative standards. The narrative ground water standard in N.J.A.C. 7:26D-2.2(a)4vi, for example, addresses both the direct contact and vapor intrusion pathways.

**N.J.A.C. 7:26E-5.6(a)** requires the person responsible for conducting the remediation to ensure that all applicable permits are obtained. For each DGW that is subject to the NJPDES rules at N.J.A.C. 7:14A-7.5(b), the person responsible for conducting the remediation must submit a DGW proposal that addresses all items listed at N.J.A.C. 7:26E-5.6(b). Pursuant to N.J.A.C. 7:26E-5.6(b)3, 4 and 8 and N.J.A.C. 7:14A-2.1(b) and 7.2, the DGW proposal monitoring plan must include adequate monitoring to evaluate and document protection of all potential receptors and compliance with the applicable conditions of N.J.A.C. 7:14A-6.2, the applicable Ground Water Quality Standards (GWQS), N.J.A.C. 7:9C, and Surface Water Quality Standards (SWQS), N.J.A.C. 7:9B.

A RAW, and thus the included monitoring plan, shall be submitted to the Department as required by N.J.A.C. 7:26E-5.5(a). The Department does not approve RAWs, other than as specified in N.J.A.C. 7:26E-5.1, however, pursuant to N.J.A.C. 7:14A-7.5(b) of the NJPDES Rules, written

Department approval for the DGW proposal, and thus the included monitoring plan, is required before any person is authorized to discharge under the PBR. A discharge can be part of an interim or a final remedial action, or part of a pilot or design study, however, in the current Technical Rules, the DGW proposal is not part of a RAW but rather is a separate submittal. The Department's approval of the DGW does not constitute approval of the RAW. The purpose of the RAW is to describe the remedial action and technology; however, when the remedial action includes a DGW, the RAW should not include all the information required to be in the DGW proposal.

A monitoring program for a pilot test or design study for a remedial action is required based on N.J.A.C. 7:26E-5.2(a)2 of the Technical Rules. However, if such tests/studies do not include a DGW, a monitoring plan submittal is not required for them except for any aspects included in a quality assurance project plan per N.J.A.C. 7:26E-1.6(a)4 and 2.2(b).

There is significant overlap of the requirements for the RAW and DGW proposal monitoring plans. There are, however, critical differences between the purposes of a performance monitoring plan in a RAW versus the monitoring component of a DGW proposal. The purpose of the RAW monitoring plan is to evaluate the effectiveness of the remedy in achieving applicable remediation standards or interim remedial action objectives, such as source removal. A remedy could not, however, be considered completely effective if it is not also protective. Thus, the RAW monitoring must also address compliance with N.J.A.C. 7:26E-5.1(d), especially when the remedy does not require monitoring under any permit. The primary intent of the monitoring plan in the DGW proposal is to evaluate protectiveness, which means evaluating any actual or potential negative impacts of the discharge; the plan should produce data that document that all receptors are protected from impacts caused by the discharge, during or following the discharge, and that approved localized or temporary negative impacts on ground water are consistent with the DGW proposal.

N.J.A.C. 7:26C-7.5(d)5 and 6 in the ARRCs require that a monitoring plan in a Ground Water Remedial Action Permit application be designed to evaluate performance optimization, plume migration or containment, effectiveness, protectiveness and the need for additional remediation.

### **3.3. GENERAL HEALTH AND SAFETY CONSIDERATIONS**

Consistent with 29 CFR 1910.120(b)(1), a site-specific health and safety (H&S) plan is appropriate for every project involving hazardous waste operations, and should address any risks resulting from implementing an in situ remedy and the associated performance monitoring program. Health and safety measures should protect all those working on a site, and all who will be otherwise using the site and adjacent property. These measures should address acute and chronic exposure to all site contaminants and materials to be handled, as appropriate, based on the duration of the remedial action. In situ remedial technologies pose some unique health and safety challenges because of the nature of some of the substances being handled, injected or

otherwise released at these sites, many of which are active industrial, commercial, or residential properties. For example, it can be very difficult to prevent “daylighting” of an injected reagent back onto the surface and difficult to predict the exact locations where this may occur.

Pursuant to N.J.A.C. 7:26E-5.1(d) any remedial action must be protective of public health, safety and the environment and N.J.A.C. 7:14A-6.2(a)7 of NJPDES specifies that “any injury to persons or property or invasion of other private rights, or any infringement of Federal, State or local law or regulations” is not authorized by any NJPDES permit. Therefore, pursuant to N.J.A.C. 7:26E-5.1(d) and 5.2(a)1 or N.J.A.C. 7:14A-6.2(a)5 and 11, any person implementing a remedial action or any discharger shall prevent or minimize any adverse effect on human health or the environment and take corrective actions to mitigate any negative effects of violating these remedial action requirements and/or general permit conditions. As such, all monitoring programs/plans required by N.J.A.C. 7:26E-5.2(a)2 and 5.5(b)6 or N.J.A.C. 7:26E-5.6(b)8 must include adequate monitoring for possible negative effects and H&S plans need to include mitigation and protection procedures adequate to prevent any injuries, exposures or damage that could lead to safety risks. They should also address immediate safety risks (e.g., trip and fall, explosive, electrical, etc.). Safety Data Sheets (SDS) for products that are part of a remedial action technology are usually available from manufacturers or providers of those products. SDS or equivalent information for all products to be used should be obtained and that data utilized in choosing appropriate protective measures for any in situ remedial action project.

## **4. SITE CHARACTERIZATION AND IN-SITU REMEDIAL DESIGN**

Site characterization is essential to determine the remediation objectives/goals and selection of the remedial approach, and ultimately for ensuring that the performance monitoring program is suitable for an in-situ remedial action. Identification of the source zone, groundwater flow direction and gradient, and the potential receptor locations is essential for the proper placement of ground water monitoring wells to be used in a performance monitoring program. Similarly, the remedial design must include performance monitoring considerations, pursuant to N.J.A.C. 7:26E-5.2(a)2, such as those discussed in the subsections below.

### **4.1. CONCEPTUAL SITE MODEL**

The CSM is a tool that can be used throughout the site investigation, remediation, and performance monitoring process to convey information and for remedial decision making. Application of the CSM is an iterative process and new information should be added when collected. In particular, if performance monitoring data indicate that the remedy is not performing as predicted, then those data should be used as the basis for reevaluating the remedy and CSM to determine the cause.

Section 5.2 of the Department's Technical Guidance for Preparation and Submission of a Conceptual Site Model ([http://www.nj.gov/dep/srp/guidance/srra/csm\\_tech\\_guidance.pdf](http://www.nj.gov/dep/srp/guidance/srra/csm_tech_guidance.pdf)) provides an excellent discussion of the types of information that should be considered when investigating a site. Key items related to performance monitoring include the following:

- soil characteristics: thickness, matrix minerals (e.g., Fe, Mn, CaCO<sub>3</sub>), organic carbon content
- geologic and hydrologic properties and dimensions of each unit of concern
- background evaluation (e.g., natural or offsite contaminant contribution)
- delineation of impacted soil and ground water media
- identification of potential sources of contamination (above and below the water table) and types of contamination
- determination of recharge and discharge areas
- evaluation of direction and rate of ground water movement
- identification of manmade structures, utilities, or historic fill
- classification of ground water
- proximity to surface water bodies
- analyze for potential sensitive receptors (only surface water bodies are currently included)
- determination if the pathway between source and receptors is potentially complete
- current plume stability (i.e., stable, shrinking, expanding, etc.).

In developing and refining the CSM and the monitoring network, the investigator should evaluate how well the known distribution of ground contaminants and significant changes in their concentrations temporally and spatially, support the current interpretation of available ground water elevation data and the assumed or predicted direction of plume migration. The investigator is also pointed to the Department's ground water technical guidance, which provides generic conceptual hydrostratigraphic models and links to additional resources that may be helpful for developing and refining the CSM.

## **4.2. REMEDIAL ACTION SELECTION AND GENERAL DESIGN CONSIDERATIONS**

In general, in situ performance monitoring is governed by the type of remedial action selected. The ability to properly monitor the performance of the remedial action should be considered during the selection and design stages. Remedial action technology screening assists the investigator in selecting a technology that will ensure protection of public health, safety and the environment, based upon careful consideration of a variety of factors. A screening process can aid in identifying viable remedial technologies for the remediation of a particular contaminated site or area of concern (AOC). Factors to be considered during the remedial action technology screening include but are not limited to the following:

- The consistency of the remedial action with applicable Federal, State, and local laws and regulations
- The ability to properly monitor the progress of the remedial action in achieving and maintaining the remediation objectives/goals
- The degree to which the remedial action minimizes risks and impacts associated with the implementation of the remedy and does not in itself adversely impact groundwater quality or other receptors
- The degree to which contaminant migration is mitigated or eliminated
- The degree to which the remedial action reduces toxicity, mobility, or volume of contaminants
- The reliability of the remedial action
- The engineering, scientific feasibility, and availability of the technology(ies) that the remedial action would employ
- Location of source material relative to the water table
- The sustainability of the remedial action with respect to energy/resource efficiency, funding availability, cost effectiveness and remediation timeline constraints. Green and Sustainable Remediation (GSR) is the site specific employment of products, technologies and procedures that mitigate contaminant risk to receptors while making decisions that are cognizant of balancing community goals, economic impacts and net environmental effects.

For a general guide to selecting compound specific remedial action treatment technologies with respect to overall costs and performance ratings, visit the Federal Remediation Technologies Roundtable (FRTR) Treatment Technology Screening Matrix at [https://frtr.gov/matrix2/section3/table3\\_2.pdf](https://frtr.gov/matrix2/section3/table3_2.pdf). Additional information on GSR is available on the EPA's website at: <https://www.epa.gov/remedytech/green-remediation-incorporating-sustainable-environmental-practices-remediation> and the ITRC website at <http://www.itrcweb.org/Team/Public?teamID=7> and other publications.

Information on the overall nature and extent of contamination across the site is critical in the design of a remedial action and the identification of the subsequent performance monitoring sampling locations. For most contaminated sites and AOCs, the CSM should be updated prior to the remedial design stage to reflect the horizontal and vertical boundaries of the contaminant plume and source zone. Obtaining this information generally requires collecting multiple samples and assessing physical and chemical characteristics of the site and the contaminants of concern. A robust CSM can greatly aid in determining the need and the location for sampling. Typical data collection needs for remedial design considerations are presented below in Sections 4.2.1 through 4.2.7.

#### 4.2.1. NATURE OF CONTAMINANTS OF CONCERN

The physical and chemical properties of contaminants of concern (COCs) for a particular site or AOC, along with the properties of geologic media and hydrologic conditions, control, to a large degree, the distribution of contaminant mass. Understanding these properties provides valuable information to the investigator with respect to the remedial action design and the associated performance monitoring program. These properties (and those of non-target COCs) affect contaminant fate and transport and may affect the ability of a given remedial technology to effectively remediate contaminants in the subsurface. Understanding these properties is also essential when determining the appropriate media for sampling, sampling locations/methodology, and analytical parameters to be included in the performance monitoring program. Chemical, physical and other natural properties of contaminants typically assessed for remedial design and which should be considered in developing a performance monitoring program include, but are not limited to the following: specific gravity, density, viscosity, vapor pressure, aqueous solubility, concentration, contaminant type (e.g., volatile, semi-volatile, chlorinated, inorganic) and degradability (e.g., attenuation and biodegradation rate constants, USEPA, 2002).

Estimates of contaminant mass and its distribution are also important remedial design considerations. The type of contaminants and their physical forms or states (e.g., separate phase, dissolved phase, vapor phase, adsorbed) will control, to a large extent, the ability of a given remedial action technology to be effective, and will also impact the development of an effective performance monitoring program. Of particular importance is recognizing the presence (or potential presence) and distribution of free and residual product. The volume of free and/or residual product must be estimated and included in the calculation of total contaminant mass in the subsurface, as this will often be a significant contribution to the total. The example below shows the significance the additional mass of 0.25 feet apparent thickness (h) of free gasoline product (specific gravity ( $\rho$ ) of 0.9) has on the total mass in a hypothetical treatment area measuring 30 feet in diameter (15-foot radius of influence) by 10 feet deep in medium sand with a soil EPH concentration of 22,000 mg/kg. Using Equation 3 of Appendix A:

First, calculate contaminant mass ( $M_{CON}$ ) in soil:

$$M_{CON} \approx 3.14159 * (ROI_P)^2 * (D_B - D_T) * (1.0 - n) * 0.02832 * 2650 * C_{CON} * 0.00000220462$$

$$M_{CON} \approx 3.14159 * (15)^2 * (10) * (1.0 - 0.35) * 0.02832 * 2650 * 22,000 * 0.00000220462$$

$$M_{CON} \approx 16,700 \text{ pounds}$$

Second, calculate mass of free product ( $M_{NAPL}$ ):

$$M_{NAPL} \approx 3.14159 * (ROI_P)^2 * (h) * (n) * (8.34 * \rho) * (7.48 \text{ gal/ft}^3)$$

$$M_{\text{LNAPL}} \approx 3.14159 * (15)^2 * (0.25) * (0.35) * (8.34 * 0.9) * 7.48$$

$$M_{\text{LNAPL}} \approx 3,500 \text{ pounds}$$

In this example, 0.25 feet of LNAPL contribute an addition 20% to the total contaminant mass to be remediated.

Any remedial approach selected must be consistent with N.J.A.C. 7:26E-5.1(e) which requires free and residual product to be treated or removed to the extent practicable, or contained if treatment or removal is not practicable. This rule provision also specifically prohibits proposing monitored natural attenuation (MNA) to address product, which necessitates a need for an active remedy. Some technologies are better suited to addressing product than others and, depending on the circumstance, the Department may not approve certain discharge proposals unless the product is first treated or removed (see Section 7). Some discharge proposals, which alone may not be approvable, may be approvable if some type of containment is proposed as part of the implementation of the remedy.

A common approach to remediate a site is the physical removal of any product through excavation, or extraction of the recoverable product by pumping or vacuuming, followed by an in situ treatment of residual product or contamination, which may otherwise represent a contaminant source for ground water, soil, indoor air, or surface water. At sites where product cannot be practicably removed or treated, a common containment method is a slurry wall and cap with temporary or intermittent hydraulic pumping to remove any contained recoverable liquid. Regardless of the chosen approach, performance monitoring points and parameters need to be selected that demonstrate whether the remedial action is successful. In particular, monitoring point location, design and sampling methodology are vital to demonstrating the success of containment.

There are many factors listed in regulation and various technical guidance documents that are considered to be indicators of free and/or residual product which may be useful aids in selecting an appropriate remedy. The investigator is encouraged to review these references when developing a NAPL remedial strategy for any given site. Some common references are provided below and in the Ground Water: SI/RI/RA Technical Guidance document.

- LNAPL Technical Guidance (2012)
- EPA Soil Screening Guidance (1996)
- EPA A Decision Making Framework for Cleanup of Sites Impacted with LNAPL (2005)
- ITRC Evaluating LNAPL Remedial Technologies for Achieving Project Goals (2009)
- ASTM E2531-06 Standard Guide for Development of Conceptual Site Models and Remediation Strategies for LNAPL Released to the Subsurface (2014)
- API Interactive LNAPL Guide Version 2.0.4
- EPA Technical Guide for Addressing Petroleum Vapor Intrusion at Leaking Underground Storage Tank Sites (2015)

- EPA Evaluation of Empirical Data to Support Soil Vapor Intrusion Screening Criteria for Petroleum Hydrocarbon Compounds (2013)

The Department considers the following factors to be potential indicators of free and/or residual product:

- Any type of separate phase contamination that is a solid, liquid (NAPL), or semi-solid that is observed directly, such as measurable product or sheen, or indirectly, such as with a hydrophobic dye or other enhanced field observation methods.
- A contaminant concentration in soil that is greater than or equal to its soil saturation limit. For example, a concentration of 111 milligrams per kilogram (mg/kg) tetrachloroethylene or 218 mg/kg of 1,2-dichlorobenzene in soil is considered to be indicative of product (See EPA’s 1996 “Soil Screening Guidance: User’s Guide”; Department’s 2013 “Development of Impact to Ground Water Soil Remediation Standards Using the Soil-Water Partition Equation” ([http://www.nj.gov/dep/srp/guidance/rs/partition\\_equation.pdf](http://www.nj.gov/dep/srp/guidance/rs/partition_equation.pdf)); “Using the Combined SESEOIL/AT123D Models to Develop Site-Specific Impact to Ground Water Soil Remediation Standards for Mobile Contaminants” (Version 2.1, May 2014) ([http://www.nj.gov/dep/srp/guidance/rs/at123d\\_guidance.pdf](http://www.nj.gov/dep/srp/guidance/rs/at123d_guidance.pdf)); and Department’s “Chemical Properties Table” (<http://www.nj.gov/dep/srp/guidance/rs/chemproperties.pdf>).
- A contaminant denser than water with a concentration equal to or greater than 1% of its water solubility (or if a mixture, greater than or equal to 1% of its effective solubility). For example, a 2,000 micrograms per liter (µg/L) concentration of tetrachloroethylene in ground water is considered to be indicative of product (N.J.A.C. 7:26E-2.1(a)14 and the Department’s “Chemical Properties Table”).
- Any organic contaminant with a concentration equal to or greater than its water solubility or effective water solubility if the contaminant was discharged as part of a mixture. For example, product is considered to be present if a concentration of 175,000 µg/L xylene in ground water is reported and the discharge was pure xylene. If the xylene was discharged as part of a mixture (i.e., gasoline) the effective water solubility of xylene may be significantly less. Effective solubility for petroleum hydrocarbon fuels can be calculated using the US EPA on-line tool at <http://www3.epa.gov/ceampubl/learn2model/part-two/onsite/es.html>.
- An Extractable Petroleum Hydrocarbon (EPH) concentration equal to or greater than 8,000 mg/kg (or otherwise indicated by the Department’s EPH Technical Guidance) and the AOC is associated with #2 fuel oil or diesel contamination. (See the Department’s EPH technical guidance on the Remediation Standards webpage at <http://www.nj.gov/dep/srp/guidance/rs/>)

- An EPH concentration equal to or greater than 17,000 mg/kg (or otherwise indicated by the Department's EPH Technical Guidance) and the AOC is associated with fuel oil #4, fuel oil #6, waste oil, crude oil, cutting oil, hydraulic oil, lubricating oil, or mineral oil. (See above referenced Department's EPH technical guidance.)

#### **4.2.2. SITE GEOLOGY AND HYDROGEOLOGY**

The properties of the geologic media, hydrogeology and otherwise remarkable subsurface features typically have a major influence on the mobility and treatability of contaminants in the subsurface. An understanding of the subsurface environment is invaluable to designing an effective remedial action and monitoring program. As discussed in the preceding section, identifying the location of free and residual product, or contaminant concentrations representative of source material, may be predicted based on the geology and hydrogeology at a site. For example, as contamination released at the ground surface migrates downward into the saturated zone, a fluctuating water table may cause a smear zone to develop, a dipping low permeability zone may cause product to migrate in an unanticipated direction, and a preferential pathway may cause contamination to migrate in an unexpected direction and at an unexpectedly rapid speed. All of these factors should inform monitoring program design.

It is not uncommon for a portion of contaminant mass to transfer from high permeability zones such as sands or a fracture to lower permeability zones such as silts, clays, and rock matrix (Parker, Chapman, and Cherry 2010; Parker, McWhorter, and Cherry 1997; Parker, Chapman, and Gilbeault 2008; Sale and Newell 2011; Suthersan et al. 2017). As such, it is important that all impacted or potentially impacted soil horizons and hydrostratigraphic units be characterized and considered as part of the conceptual site model. Examples of key characteristics to consider include soil type, effective porosity, permeability, grain size, bulk density, fraction organic carbon, lithology, formation strike and dip, faults and fractured zones, aquifer thickness, hydraulic conductivity, ground water velocity, ground water flow direction, seasonal and anthropogenic water table elevations, and preferential pathways (such as pipelines, utility corridors/trenches, a coarser channel deposit in otherwise finer grained sediment).

Just as site geology controls the initial discharge and subsequent contaminant migration, geology will also influence or exert control over the propagation and distribution of treatment solutions, slurries, and gases (i.e., fluid) injected or released into the subsurface. In both high and low permeability zones, design of the delivery system needs to account for these influences to maximize fluids coming into contact with target contaminants and to reduce the potential for contaminant rebound. For the purposes of this section it is recognized that the placement of solid treatment material into the subsurface may result in amended ground water quality that will serve as the treatment fluid.

While not required, in many cases a pilot test or design study may be an appropriate means of evaluating the effect of site geology on fluid distribution in the subsurface. The pilot test should

be designed to determine injection well radius of influence versus injection rate, as well as technology effectiveness.

As used throughout this section, the term radius of influence is not meant to imply a circular pattern. Measurements should be taken in multiple directions and varied depths from injection wells to understand how potential anisotropy of the subsurface influences the radius of influence. When designing the layout of a multi-injection point system, ideally, the radius of influence of the injection points should overlap, horizontally and vertically as necessary, so that the entire intended zone of treatment is effectively covered. Subsurface heterogeneities should be accounted for when selecting performance monitoring locations. It should be anticipated that the radius of influence will be greater in higher permeability zones and smaller in the lower permeability zones. For fluid injections, ITRC (Interstate Technology & Regulatory Council 2005) states that the radius of influence can vary from “2.5 feet for tight clays to 25 feet in permeable saturated soils.” The investigator will need to monitor the volume of fluids delivered during any injection event to prevent fluids from daylighting on the surface.

Regardless of whether or not a pilot test is conducted, several important fluid delivery design considerations for different geologic units are provided below.

- **High permeability soils/fill.** High permeability soils typically require a high volume of fluid to be introduced into the subsurface for effective distribution/contact with contaminants. The investigator is referred to Appendix A for calculations to determine the minimum volume of fluid required based on the target zone of treatment. While injecting a sufficient volume of fluid to address the calculated contaminant mass in one injection event may be possible in a high permeability formation, in many cases this is not an effective approach due to rates at which many contaminants desorb from the soil matrix. Delivery of fluid during multiple events typically increases the potential for and duration of contact between the fluids and target contaminants, resulting in improved remedial effectiveness. Although high permeability formations typically have the ability to readily accept fluids and larger radii of influence can be achieved, it is important not to underestimate the number of injection wells required to effectively distribute the calculated volume of fluids throughout the target treatment area. As treatment fluids travel further from the injection well, reactions and dilution will result in lower amendment concentrations that may be insufficient to treat the target contaminant mass.

Treatment reagent solutions/slurries injected into high-permeability, granular soils tend to infiltrate the pore space/voids more uniformly when a sufficient quantity of solution/slurry is injected and the duration of the injection is sufficiently long.

- **Low permeability soil.** Low permeability soils can typically accept significantly less volume of fluids during each injection event than high permeability soils. Preferential flow pathways are likely to form due to increased pressures typically applied to assist in the delivery and distribution of the fluids. These injection pressure-induced flow paths

may be different than contaminant migration pathways that evolved without the influence of pressure injection. The most effective fluids delivery systems will typically include closely-spaced injection wells that will promote distribution of injectants through the subsurface via the same pathways as contaminant migration. Desorption of contaminants from the soil matrix may be slower than in higher permeability soils, as such the effective volume of fluids delivered per injection event will be reduced, resulting in the need for more injection events. Another method to address contamination in low permeability soils include use of a gaseous reagent, such as ozone. This is suggested by ITRC (2005) because of a greater gas phase permeability, relative to water permeability. Use of hydrofracturing is another method to increase permeability, but a thoughtful approach is needed to try to maximize fracturing in the area of contamination, without causing the spread of contamination.

Low-permeability soils/geologic formations tend to exhibit soil-structures that may act as preferential pathways for contaminant and /or reagent migration. While continuous soil cores should be obtained and inspected/logged in detail as a matter of routine, it is particularly important in low permeability soils to identify the presence of soil structures that can act as preferential pathways.

Examples of soil structure include: vertical and horizontal joints/fractures; prismatic structure; blocky structure; thin sand beds; cracked and fractured ironstone beds; cracked and fractured siderite-cemented zones; etc.

The Woodbury Formation, for example, is composed primarily of clayey silt and silty clay. However, fracturing/jointing is widespread within the Woodbury Formation, varying in intensity from place to place. In some areas, joints are open and mineralized and provide pathways for water and contaminant migration. At one site investigated by the Department, free-phase diesel fuel migrated several hundred feet from a leaking UST through a highly fractured/jointed area of the Woodbury Formation to a nearby creek. Test pits excavated using a backhoe showed the upper eight to ten feet of the Woodbury Formation at this location contained a large number of sand-filled high-angle joints/fractures; sand had infiltrated the joints/fractures from the overlying sandy soil zone.

- **Histosols (peat / marsh mat).** Histosols are characterized by high organic carbon content and poor drainage. The high organic content may create additional fluid demand. When the chosen fluids have the potential to react with or be consumed by the organic material in the soils, the investigator is encouraged to analyze soils for organic carbon in addition to target contaminants, so the additional fluid demand can be calculated and incorporated into the remedial design. The poor drainage typical of histosols often results in significant limitation of the volume of fluids that can be delivered during each injection event. While monitoring the volume of fluids discharged is needed for any injection to prevent daylighting, it is a particular concern for histosols.

- **Heterogeneous soils.** Heterogeneous soils present significant challenges to remedial design. While contaminants may have migrated primarily through the higher permeability soil features, the lower permeability soils typically exhibit a greater ability to retain many contaminants. The result is retention of contaminants in soil features that have limited accessibility to injected materials due to the preferential flow of the fluids through the higher permeability soils. In heterogeneous formations, site characterization is even more critical to determine more precisely where the contaminants are located relative to the various geologic features, so that those areas can be targeted for remediation.
- **Bedrock Formations.** Ground water flow in bedrock formations is primarily fracture and bedding plane controlled, although weathering and mineral dissolution may add additional pathways. Detailed site characterization is required to determine contaminant distribution and migration pathways and subsequently injection well design and location. The investigator is reminded that in sedimentary rock formations, contaminant mass may be primarily held within the lower permeability rock matrix, as opposed to the local fracture system. Matrix porosity may be up to four orders of magnitude greater than fracture porosity and it is not uncommon to lose NAPL in fractures to the rock matrix by dissolution and diffusion (Parker et al. 2010). As stated by Lipson et al. (2005), the fractures are the conduits for ground water flow, but the rock matrix is the reservoir for contamination. As a result, depending on the equilibrium condition of the plume, monitoring points that draw a ground water sample predominantly from the rock matrix, may detect significantly higher concentrations than wells that draw water moving more rapidly through zones of secondary porosity. Injection volumes and extent of influence will vary significantly based not only on the specific bedrock formation, but also on the specific treatment, rendering site characterization and pilot testing critical to developing an effective treatment plan. An in situ treatment may be successful in treating ground water in the fractures, but unless contaminants within the rock matrix are also addressed, the clean water in the fractures may be re-contaminated. The investigator should consider the rate of diffusion from the rock matrix and ground water flow velocity when designing a treatment plan and performance monitoring program. Most of the monitoring issues and concerns discussed above for heterogeneous areas apply equally to bedrock formations.

In remedial design, the goal should be to maximize the likelihood of delivering treatment fluids to where the target contaminant mass exists, while avoiding higher permeability zones that could carry amendments away from the target treatment area. While this is a common problem in heterogeneous soils and bedrock, it can also be an issue in more homogenous type soils, particularly when a preferential pathway is present, such as an underground utility or pipeline, etc.

To encourage longer contact time with contamination in a finer grained matrix, the investigator may consider using a viscous reagent and increasing the discharge duration in locations proximal to areas of high contaminant mass. Another methodology is pulsed pumping, where the pump used for the injection is cycled on and off causing a back and forth motion to the reagent, which may improve contact with the contamination (Gale et al. 2015).

#### **4.2.3. GENERAL IMPLEMENTATION CONSIDERATIONS**

The investigator should consider the location of the treatment area with respect to on-site and off-site structures such as buildings, roads, water bodies, overhead and underground utilities, etc. that may result in access limitations or damage to the structures. Such issues may inhibit the ability of a given remedial technology to effectively remediate a contaminant plume or area of soil contamination.

Performance monitoring in areas of limited access can be difficult and sometimes an alternative assessment method is needed. When off-site access is needed or relocation of utilities is necessary, sufficient time for these activities needs to be accounted for when developing an implementation and sampling schedule.

The proximity of manmade structures to the treatment area and potential negative effects on any nearby structures (e.g., increased corrosion, vapor accumulation, and/or soil erosion), should be considered and prevented or mitigated as necessary to comply with N.J.A.C. 7:14A-6.2(a)7, N.J.A.C. 7:26E-5.5(b)10 and N.J.A.C. 7:26E-5.7(b)9, where applicable.

While viable remedial action technologies may be identified for the contaminants in the area of concern, the investigator should evaluate how other factors, such as extreme cold or hot temperatures, severe storms, sale or redevelopment of the property, etc. could impact the treatment and monitoring program.

The treatment area may include all or a portion of the contamination, but in no circumstance, should a proposal be submitted that only focuses on treating specific individual wells, while leaving contaminant mass outside of the individual wells unremediated, unmonitored or otherwise unaddressed. Possible exceptions would be if the discharge is part of an interim remedial measure (IRM) or pilot study. In these cases it should be clear that the intent of the investigator is to address the entire source area at some point prior to case closure. It is unacceptable to claim successful remediation of a large source area by focusing treatment only on individual wells.

Care should also be taken to ensure treatment of the aquifer or saturated zone in an area of concern, and not to inadvertently treat the monitoring wells themselves. For instance, high pressure injection of powdered activated carbon (PAC) has been shown to preferentially migrate from injection borings through induced fractures to monitoring wells where it can be lodged in the sand pack surrounding the well screen and/or the well itself. Samples collected from such

wells yield a false indication that the aquifer/saturated zone has been remediated, when in actuality only the ground water in the well itself has been remediated (Fox, 2015 and [www.regenesis.com/pac-liability](http://www.regenesis.com/pac-liability) <http://www2.regenesis.com/liability-remediation-using-powdered-activated-carbon-high-pressure-injection>).

#### **4.2.4. TECHNOLOGY SPECIFIC CONSIDERATIONS**

Many remedial actions may require evaluation of data specific to a given remedial technology prior to selecting and completing a design. The following presents a partial list of the characteristics that may be considered for specific types of in situ remediation.

##### **4.2.4.1. AEROBIC AND ANAEROBIC BIOLOGICAL PROCESSES**

Specific data needs for in situ technologies utilizing aerobic or anaerobic biological processes should be understood for the effective design and implementation of a remedial action. Soil and/or groundwater data which may be important to a given design include biogeochemical parameters (such as total organic carbon (TOC) nitrates, sulfates and microbial population), field parameters (such as dissolved oxygen (DO), pH, oxidation reduction potential (ORP)) and contaminant composition and concentration. For the purposes of a remedial design, bench scale and/or pilot scale testing may be warranted to assess the following: effectiveness of reagent(s) well yield, distance-drawdown relationships, radius of influence (ROI), biogeochemical soil/formation demand for specific substrates injected into the area of concern, presence of desired microorganisms, etc.

##### **4.2.4.2. PHYSICAL AND CHEMICAL PROCESSES**

A wide range of in situ remedial action technologies use and combine these types of processes, which include solidification, stabilization, soil flushing, surfactant injections, soil vapor extraction, air or oxygen sparging, and chemical oxidation and reduction. Design considerations for these processes may include the same biogeochemical parameters as listed above, plus contaminant mobility, solubility, vapor pressure, reactivity, non-target COCs, well yield, distance-drawdown relationships, ROI, leachability, etc.

##### **4.2.4.3. THERMAL PROCESSES**

Data needs for in situ thermal technologies (e.g., electrical resistance heating, steam enhanced extraction, and thermal conduction heating) include an understanding of groundwater flux (elevation and flow direction), groundwater velocity, hydraulic conductivity, concentrations of major anions and cations in groundwater, temperature, and changes in contaminant characteristics related to temperature.

### **4.3. INTEGRATING TREATMENT DESIGN AND DOSING WITH PERFORMANCE MONITORING**

The items presented below should be considered during treatment design and treatment performance monitoring, and are applicable to a wide array of treatment scenarios/techniques, such as injection wells (whether single wellheads or manifolded systems), direct-push technologies, injection trenches and application into open excavations. These techniques may be associated with many possible processes such as in situ aerobic and anaerobic biological processes, in situ physical and chemical processes, and in situ thermal processes. To be effective, the treatment reagent must be distributed in the subsurface and brought into direct contact with the contaminant(s). A suitable performance monitoring well network and, where appropriate, a suitable monitoring sensor network should be devised in order to monitor process quality control during implementation and to confirm the effectiveness of the treatment post-implementation.

#### **4.3.1. INJECTION WELLS AND MONITORING WELLS**

There is a distinction between injection wells and monitoring wells. While the two types of wells may be similar in design, they serve distinctly different purposes. The purpose of an injection well is to deliver reagents to the subsurface. The purpose of a monitoring well is to monitor groundwater quality.

When designing the layout of the treatment distribution system, whether vertical or horizontal injection wells, borings or trenches are to be used for in situ remediation, the overlap of the planned radius of influence of the injections with the location of existing monitoring wells should be evaluated. Data collected from monitoring wells within the ROI may not be representative of overall long-term ground water quality. Therefore, where possible, the location of injection wells/units should be chosen to avoid compromising any existing monitoring wells. When this is not possible, replacement monitoring wells should be included in the remedial design.

The investigator may wish to consider the use of wire wrapped injection well screens as opposed to slotted screens due to their significantly increased open area and in order to avoid potential issues with corrosion resulting from injection of various reagents.

Injections into monitoring wells are not recommended; this includes the deployment of oxygen releasing compound socks. However, there may be some instances where converting source area monitoring wells into injection wells could optimize the remediation. In the event that injections are needed directly into or in close proximity to existing monitoring wells, these wells may no longer be suitable for compliance monitoring because ground water samples collected from them are typically no longer representative of overall ground water quality in the plume or in the formation. In such instances, although it may be necessary to install separate compliance

monitoring well(s), utilizing injection wells or monitoring wells within the ROI as “process” monitoring wells may be useful to confirm concentrations of constituents injected and residual contaminant concentrations.

Department unregulated heating oil tank case files provide two specific examples of how monitoring wells were compromised by injection activities that affected the representativeness of ground water samples and physical efficiency of the wells.

In the first example, treatment reagent(s) slurries remained in monitoring well screens and sand-packs for more than a year. Although the results of ground water samples from these wells were compliant with the GWQS, based on further investigation, ground water in relatively close proximity to these wells remained contaminated.

In the second case, injecting oxidizing and oxygen-releasing solutions and slurries very close to monitoring wells, appeared to oxidize dissolved iron and manganese in the ground water and formed precipitates that plugged the monitoring well screens and sand packs. This reduced ground water flow through the screens, rendering the wells less effective for future monitoring or injection.

To avoid or minimize these types of problems, the investigator should determine the following information and use it in evaluating the ROI of injections:

- 1) total mass of site contaminants and competing reactants (such as native oxygen demand, geochemistry, etc.) in target injection areas.
- 2) amount of treatment fluid required to address the target mass of site contaminants.
- 3) number of injection and performance monitoring wells.
- 4) anticipated volume of injectant necessary at each location to attain the remedial objective, calculated using subsurface properties determined during the site characterization.
- 5) number and frequency of injection events.

Equations that can be used to determine the above information, and that can be used to verify that the in situ injections were performed as proposed/designed, are presented in Appendix A. Site-specific porosity ( $n$ ), hydraulic conductivity ( $k$ ) and fraction organic carbon ( $foc$ ), and treatment reagent(s) viscosity ( $\mu$ ), should be used in these calculations whenever possible, however this appendix also includes literature values for some of these parameters.

To aid the investigator in monitoring, evaluating and/or documenting the effectiveness of the remedial action, a detailed field-log of each injection location should be prepared. The log should document whether the calculated mass, volume, solution/slurry concentration and duration of injection were attained at each injection location. Appendix B includes

recommended items to be included in these field logs for two general types of injection events. Section 3.5 of the Department's Soil Technical Guidance ([http://www.state.nj.us/dep/srp/guidance/srra/soil\\_inv\\_si\\_ri\\_ra.pdf](http://www.state.nj.us/dep/srp/guidance/srra/soil_inv_si_ri_ra.pdf)) and Chapter 10 of the Department's Field Sampling Procedures Manual (FSPM) (<http://www.nj.gov/dep/srp/guidance/fspm/pdf/fsmp2005.pdf>) can also be referenced for additional information regarding field documentation.

#### **4.4 PILOT TEST/DESIGN STUDY**

Pilot scale field tests and/or design studies can play a critical role in designing a full-scale remedial action with an effective monitoring plan. Pilot tests or design studies are utilized to determine if a technology will be used for a final or full-scale remedial action. A pilot study is a remedial action typically conducted on a portion of the impacted area. Pilot studies are conducted to determine the effectiveness of a remedial action or technology for COCs within a treatment area. The pilot study is performed to determine design criteria such as radius of influence, well point spacing, injection/recovery flow rates, viability of selected technologies and potential secondary impacts on groundwater quality and receptors. The pilot study is also useful in predicting full-scale remediation costs. In most cases, such tests or studies should be completed prior to RAW submittal since their results are to be included in the RAW per N.J.A.C. 7:26E-5.5(b)4.

Pilot studies are typically performed in a location that is representative of site conditions. If site conditions in the treatment area vary beyond the study area, expansion of the pilot study may be warranted so that sufficient data is collected for the design of a remedial action across the varied conditions. If the entire plume will not be treated in the remedial action, it may be appropriate to choose a side gradient portion of the contaminant plume for the study to observe the potential for COCs to migrate back into a treated area and/or the effect of the remedial action on unaffected/down gradient areas of the site.

Additional detail about pilot testing is outside the scope of this technical guidance, however additional information may be obtained from sources such as EPA, ITRC, and technology vendors.

### **5. GENERAL PERFORMANCE MONITORING OBJECTIVES**

This section of the technical guidance focuses on defining remedial goals and performance objectives and introduces the concept of using performance metrics to evaluate the effectiveness and efficiency of in situ remedial action(s) in meeting remedial action goals and performance objectives applicable to a site. In order to determine performance monitoring objectives, the investigator should ensure that site conditions are well understood within the vicinity of the treatment area, an adequate monitoring network exists and the selected treatment is appropriate

for contaminants to be remediated. Therefore, this technical guidance should be used in conjunction with other related Department technical guidance in the SRP Guidance Library.

## **5.1. OVERVIEW OF PERFORMANCE MONITORING**

Monitoring may be viewed as the collection and analysis of repeated observations or measurements to evaluate changes in condition and progress toward meeting a performance objective (EPA, 2004). Monitoring should include the collection of field data (i.e., chemical, physical, and/or biological) using appropriate sampling methods over a sufficient period of time and frequency to determine the status at a particular point in time and/or trend over a period of time in a particular environmental parameter or characteristic, relative to clearly defined performance objectives. The data, methods, and endpoints should be directly related to the remediation performance goals and objectives to reach the regulatory requirements for the site.

Performance monitoring for in situ remedial action involves the collection and evaluation of data both during and following treatment, and the comparison of that information to pretreatment or baseline conditions and ultimately to any applicable regulatory standards. This technical guidance distinguishes between two types of performance monitoring: system efficiency or process monitoring; and remedial effectiveness monitoring (ITRC, 2004). For the purposes of this technical guidance, system efficiency or process monitoring is considered to be monitoring performed during treatment to optimize the in situ remedial process; remedial effectiveness performance monitoring compares conditions before and after treatment using various performance metrics (see Section 5.3) to determine if remedial performance objectives have been met. The detailed design of the monitoring plan depends on site-specific conditions and the remedial technology applied. Sections 5.4 and 6.0 provide more detailed guidance.

The investigator can use this technical guidance document to identify clear, measurable remedial goals and site-specific performance objectives, as well as the metrics and tools, to measure performance toward meeting these objectives for inclusion in a DGW proposal and RAW.

## **5.2. IDENTIFY REMEDIAL GOALS AND PERFORMANCE OBJECTIVES**

The ultimate goal of remediation is to meet numeric and narrative Remediation Standards, (N.J.A.C. 7:26D) and, if applicable, compliance with any other federal, state, and local requirements (e.g., N.J.A.C.7:26E-5.1 and 7:14A-7.2(a)). This is considered the long-term goal. However, achievement of interim site related remedial milestones may be needed to reach the long term goal.

Examples of interim site-related remedial milestones include the following:

- preventing further exposure to contaminants

- preventing further migration of contaminants from source areas
- achieving the ecological risk-based remediation goal established pursuant to N.J.A.C. 7:26E-4.8 for soil or sediment
- reducing concentrations of contaminants outside the source zone
- preventing further migration of the groundwater contaminant plume
- depleting the source and dissolved contaminant levels sufficiently to allow for natural attenuation
- reducing the mass discharge rate or flux emanating from the source (USEPA 1999, ITRC 2004 and ITRC 2010).

It should be noted that per N.J.A.C. 7:26D-2.2(b) and 3.2(b), the Department does not approve ground water or surface water remediation standards based on site-specific risk assessment and there is no regulatory basis for developing alternate (i.e., site-specific standards) for Class I or II-A ground waters.

When remedial goals are referred to as ultimate or final, they are usually based on regulatory or statutory requirements. In contrast, remedial performance objectives may include site-specific goals, and may also include interim site related remedial milestones or measurable remedial results that are not general or specific rule requirements, but will further the attainment of the remediation goals.

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

Remedial goals and site-specific performance objectives should be defined during the RAW development and/or in the DGW Proposal. Regardless, remedial performance objectives should be established based on the conditions identified in the CSM (see Section 4.1) and periodically re-evaluated based on actual field data, as the remedial action progresses. Remedial performance objectives can also be used as part of implementation of a multi-component remedy and decision-making process, such as when to transition from one treatment technology to another, and when the site is transitioned from active remediation to MNA.

The investigator can use various approaches to set remedial performance objectives. At some sites, it is possible to apply aggressive treatment of the source zone and dissolved phase and attain remedial objectives relatively quickly. At other sites, it may take much longer. For example, the timeframe to attain the remedial objective could be different for a source zone than for the downgradient aqueous-phase plume. Additionally, a remedial approach could be designed

to stabilize or treat the plume and control associated risks first, with reduction of mass discharge from the source zone as a subsequent remedial performance objective. Reduction of mass discharge could be achieved using treatment, partial removal, or containment of the source. This approach could result in remediation of a large portion of the plume, while the inherently difficult source remediation is addressed separately. Similarly, it may be necessary to immediately address receptor impacts such as vapor intrusion, while plume remediation continues over a much longer timeframe.

Additional examples of site-specific performance objectives include, but are not limited to the following:

- Initial treatment to address IEC or removal of receptor pathway
- Contain or mobilize contamination with placement of engineering controls
- Remediate contaminated ground water to concentrations that allow natural attenuation to address the remaining levels
- Remediate to meet the groundwater Vapor Intrusion Screening Levels
- Eliminate vapor intrusion or surface water impact with engineering controls
- Injections to treat dissolved VOC plumes and contaminated soil to prevent significant plume and/or vapor displacement into clean areas or into areas where potential receptors could be impacted. For injections of amendments to treat primary ground water contaminants of concern, minimize or prevent long-term, direct or indirect negative secondary impacts on ground water from the amendments themselves

### **5.3. PERFORMANCE METRICS**

Development of an effective monitoring approach to evaluate the baseline and progress towards achieving remedial objectives is a critical element of an in situ remedial action. As such, the monitoring approach should include a spatially and temporally sufficient and reliable data set measuring performance of the remedy. This section provides technical guidance and supporting material to assist the investigator in developing a monitoring approach that evaluates remedial performance towards achievement of site-specific remedial objectives.

The investigator should also identify the metrics and parameters proposed to measure remedial action performance in meeting remedial goals and objectives. One or more “performance metric(s)” should be defined for each remedial objective. Performance metrics are measurable characteristics that relate to the remedial progress of a technology in meeting remedial performance objectives, and should be defined in terms of the technology(ies) being used, targeted media, location of sensitive receptors, and the expected response of the subsurface to treatment, which is often technology-dependent (ITRC, 2004 and 2009). A USEPA expert panel on dense non-aqueous phase liquid (DNAPL) remediation found that, “no single metric by itself is likely to be adequate for assessing the performance and potential benefits of (in situ) technologies; thus, conjunctive use of multiple metrics should be used to evaluate performance”

(U.S. EPA, 2003). Every metric has limitations; by monitoring several metrics, a clearer picture of progress can emerge. Examples of metrics in performance monitoring include the following:

- mass flux
- quarterly analytical sampling
- pilot test results
- success of treatment as measured by select performance treatment parameters (e.g., soil sampling results, reduction in plume boundary or source material)

Identification and selection of applicable performance metrics and preparation of the performance monitoring plan are discussed further in Sections 5.4 and 6.0.

There are sites where the applicable remediation standards cannot be achieved because of complex geological and hydrological conditions, technological limitations, contaminant physical properties, and chemical distribution. At these sites, an evaluation of performance monitoring results may indicate modifications to the remedial objectives or remedial technology may be necessary. Performance monitoring may indicate that ground water remains above the applicable remediation standards and cannot be remediated due to technical impracticability (e.g., a case with high concentrations of chlorinated compounds where it may be technically impracticable to achieve the applicable ground water remediation standards). Even in cases deemed technically impracticable, continued performance monitoring is typically necessary to document continued protectiveness of public health and safety, and the environment. Refer to the Department's Technical Impracticability Guidance for Ground Water ([http://www.nj.gov/dep/srp/guidance/#tech\\_impracticability](http://www.nj.gov/dep/srp/guidance/#tech_impracticability)).

#### **5.4. PERFORMANCE MONITORING PLANS FOR REMEDIAL ACTION**

An effective performance monitoring plan considers a number of different factors, all of which require the investigator to have an understanding of the site, the associated CSM and the overall remediation goals and objectives. Major factors to consider are: location of the treatment area, contaminant mass flux, position of monitoring wells; the timing of sampling; the frequency of sampling; the composition of the remedial additive being discharged (if any); and what constituents are being analyzed via field or laboratory analysis and the potential for impacts to receptors. This section of the technical guidance describes development of performance monitoring plans for groundwater, soil, surface water/sediments, and indoor air. Multiple references for performance monitoring are available in the Reference Section of this document.

The Technical Rules include performance monitoring requirements for both NJPDES DGW proposals (N.J.A.C. 7:26E-5.6(b)) and RAWs (N.J.A.C. 7:26E-5.5(b)). The general and specific remedial action requirements of N.J.A.C. 7:26E-5.1 and 5.2 are applicable to development of performance monitoring for both a DGW Proposal and a RAW.

According to the Technical Rules, if the remedial action requires a NJPDES DGW PBR, a DGW proposal to request use of the PBR shall include a “monitoring plan, including but not limited to, the monitoring wells to be sampled, the frequency of sampling for wells, and if applicable, monitoring of the fluid to be discharged, a list of all the analytes to be monitored, and a schedule for the submission of sampling results” (N.J.A.C. 7:26E-5.6(b)8). This requirement applies to both pilot-testing and full-scale implementations and can be part of either process or effectiveness monitoring. Consistent with N.J.A.C. 7:14A-2.1(b) and 6.2(a)7,11, and 14, the purpose of the monitoring plan for the DGW proposal is to evaluate any actual or potential negative impacts of the discharge and document that all receptors were or will be protected throughout the duration of the impacts of the discharge.

For most sites, the Technical Rules require a RAW be submitted to the Department for each area of concern and the RAW shall include “a plan to evaluate the effectiveness of the remedial action” (N.J.A.C. 7:26E-5.5(b)6). If a final remediation document for unrestricted use is filed with the Department within one year after the earliest applicable requirement to remediate, a RAW is not required.

To aid the investigator in development of the DGW proposal and RAW monitoring plans, Section 6 includes six detailed monitoring parameter tables for the specific technologies, as well as Tables 1, 2, 5, 6, 7, and 8. Each table lists standard field parameters typically included for all ground water sampling events.

For the monitoring plan included in the DGW proposal, these tables in Section 6 identify parameters generally required for all DGW permits (Note 1). The investigator, however, should use the above-specified purpose of the DGW proposal monitoring plan (i.e., regarding negative impacts and receptor protection) and Notes 2 and 3 to guide their selection of the full parameter list. The number and locations of monitoring points and which media to monitor should also be based on the purpose specified above for the DGW proposal monitoring plan.

For the RAW, these tables indicate which parameters are recommended (Note 2) vs. conditional (Note 3) for the particular technologies indicated by the name of a table and for various sampling media (i.e., ground water, soil, soil gas).

“Conditional analysis” (Note 3 in all tables) refers to parameters that may or may not be important or useful to include depending on site-specific conditions or the remedial objectives. For example, when monitoring a remedial action to treat VOC contamination that is within historic fill, or in a formation with naturally occurring arsenic or other metals, it may be important, depending on the technology and site setting, to evaluate secondary impacts on ground water and/or surface water from metals. Another example is that it may be appropriate for an investigator to include a more comprehensive list of parameters and/or additional media in a monitoring plan for an active remedy designed to allow a LSRP to issue an Unrestricted Use RAO verses a plan for an active remedy with a remedial objective to reduce contaminant mass sufficiently to allow MNA to achieve final remedial goals.

In addition to the Section 6 tables, the investigator should use the subsections below, general guidance in Sections 5.2 and 5.3 above, the technology specific Sections 6.2 through 6.4, and Section 7.1, in determining monitoring parameters, which media to monitor, and all other aspects of the applicable monitoring plan.

When preparing a RAW for Unregulated Heating Oil Tank (UHOT) cases, the investigator should discuss the proposed post remedial soil and/or ground water sampling with the assigned Bureau of Field Operations (BFO) case manager prior to implementing any sampling.

Appendix C of this technical guidance presents a list of reagent products commonly used for in situ remedial action technologies that utilize biological, physical, and/or chemical processes. It indicates which table(s) in Section 6 are the most applicable for the reagents listed in the appendix. This appendix also includes suppliers, trade names and additional information about certain products. Inclusion of a product in Appendix C does not imply Department endorsement of any kind and the Department welcomes all suggestions for corrections, appropriate additions, deletions, and ongoing updates to Appendix C as remedial action technologies are changed, become obsolete, or new ones are developed.

#### **5.4.1. PERFORMANCE MONITORING FOR IN SITU GROUND WATER REMEDIATION**

Performance monitoring points and wells should be located and designed to evaluate the performance of the remedy and to document protection of receptors. If the final remedial goal is MNA, the performance monitoring well network should be installed consistent with the Department's Monitored Natural Attenuation Technical Guidance and the Ground Water: SI/RI/RA Technical Guidance. Monitoring point design should consider subsurface heterogeneities, with respect to construction of the points or wells in zones of varying permeability. For example, a depth discrete sampling approach, such as a direct push method can target a small vertical interval within either a highly permeable or a lower permeable zone, however, if a monitoring well is screened across both types of zones, a sample from it is likely to be predominantly from the higher permeability zone. It may be possible to obtain depth discrete samples from such a well using alternate sampling methods such as passive diffusion bags but vertical profiling and/or vertical flow measurements may be needed to determine how to appropriately interpret the data. See Section 6.9.2.5 of the Department's Field Sampling Procedures Manual (<http://www.nj.gov/dep/srp/guidance/fspm/>) and ITRC's "Protocol for Use of Five Passive Samplers to Sample for a Variety of Contaminants in Groundwater" (<http://www.itrcweb.org/GuidanceDocuments/DSP-5.pdf>) for additional information.

Additionally, consistent with the Department's Field Sampling Procedures Manual (6.9.2.5.1.7), vertical profiling is required, at least during the initial depth discrete sampling event when a well has more than five saturated feet of screen and future depth discrete sampling is planned. Additional profiling events may be warranted to verify that conditions have not changed and that the chosen sampling intervals remain appropriate. If depth discrete sampling is used during or

immediately after an injection event, it is recommended that vertical profiling be conducted of any wells in the immediate vicinity of the treatment area when more than five saturated feet of screen is present, since the discharge may have impacted flow regimes and contaminant distribution. ITRC also has information available on use of direct push wells, in its document “The Use of Direct-Push Well Technology for Long-term Environmental Monitoring in Groundwater Investigations” located at [http://www.itcreweb.org/GuidanceDocuments/SCM\\_2\\_ForWeb.pdf](http://www.itcreweb.org/GuidanceDocuments/SCM_2_ForWeb.pdf).

For reasons described in Section 4.3.1, monitoring points and wells used to monitor the performance of an in situ remedial action in meeting final remedial goals should ideally be located no closer to the treatment zone, e.g., injection wells/trenches, than the designed “radius-of-influence” for those injection units. Use of such a rule of thumb for locations of monitoring wells provides more assurance that the remedial action is addressing the entire contaminated plume. Monitoring wells located within that radius may only reflect impacts on the ground water resident in the monitoring well itself and in its immediate vicinity, thus consecutive, compliant ground water samples from such wells could be misleading.

As discussed in the Department’s Ground Water: SI/RI/RA and MNA Technical Guidance documents, monitoring wells are typically categorized as source area, contaminant plume/plume fringe area, sentinel, and background wells (depicted in Figure 1). Performance monitoring may also include wells in transects which are perpendicular to the groundwater flow direction to monitor lateral components of the plume and to evaluate mass flux over time (ITRC 2010 and API 2003). Intermediate and/or deep wells may be necessary to evaluate the vertical extent of the plume. The investigator is reminded that preferential pathways and heterogeneities, regardless if manmade or natural, may affect ground water flow. It is critical that the investigator have a firm understanding of the subsurface stratigraphy to reduce the likelihood of a flawed conceptual site model, so that a competent monitoring well network considering well location, vertical interval to monitor and sampling methodology can be developed. In addition, the investigator should evaluate the distribution and any significant temporal/spatial changes in COC concentrations, and assess whether that data supports the current interpretation of available ground water elevation data, the assumed ground water flow direction and predicted route(s) of contaminant transport. The ground water sampling method used and any changes in methodology over time should be taken into consideration when evaluating site data and the conceptual site model.

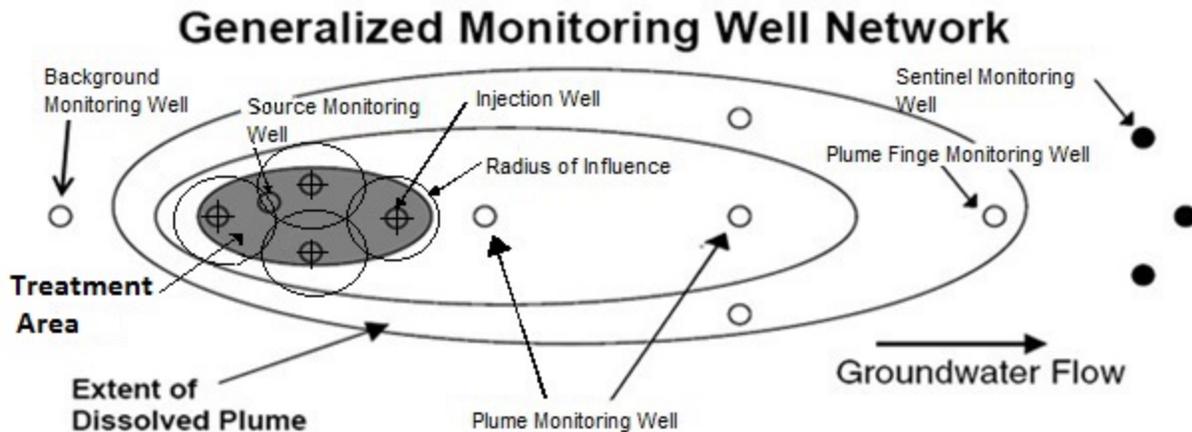


Figure 1. Generalized monitoring well network

The following categories of wells should be included in the performance monitoring network:

Source Area Monitoring Wells

Source area monitoring wells may include a single monitoring well or multiple monitoring wells, to monitor the remedial effectiveness within the source area. The number, location, and construction of monitoring wells should be dependent upon the characteristics of the source area. The source area monitoring wells should not be used as injection wells for in situ remediation technologies except as noted in Section 4.3.1. However, as also noted in Section 4.3.1, useful information may be obtained in some instances by sampling injection wells. Information obtained by sampling one or more existing wells using different sampling methods at about the same time may prove useful in designing a monitoring network. For example, if the traditional high purge rate sampling yields significantly higher concentrations of VOCs from a well than low flow sampling yields, this could be an indication of the proximity of the well to a source area. Such results may indicate that additional investigation near the well is appropriate and an additional well could be installed closer to the source or that the well should be replaced with a multi-well cluster with shorter screens at different vertical intervals.

Plume Area and Plume Fringe Monitoring Wells

Plume area monitoring well(s) should be located outside the aerial extent of the source area and within the contaminant plume. An understanding of ground water flow direction is important so that wells can be located along contaminant flow path(s). In cases where there may be significant variations in contaminant flow, the location of the plume monitoring wells should account for any such changes. Plume fringe monitoring wells should be located to monitor the horizontal and vertical contaminant concentrations at the leading, lateral and vertical edge(s) of

the contaminant front. If the zone of treatment extends beyond the source area, there should be a sufficient number of plume and plume fringe area monitoring wells such that some wells are located within the anticipated radius of influence and some are located outside that radius. Bear in mind, the injection itself may cause mounding of the water table, which could affect the radius of influence and zone of treatment.

With any type of in situ treatment, it is generally best to have at least one plume area well immediately down-gradient of the treatment area and outside of the ROI. Other lateral and vertical sample locations, depending on the size and scope of treatment may also be needed to identify and monitor any expected or unexpected issues associated with the treatment.

### Sentinel Wells

If the installation of sentinel wells (up-gradient, lateral, down-gradient, vertical) is necessary, the wells should be located to detect migration of the contaminant plume toward the nearest unimpacted receptor and to allow sufficient time for a remedial response to be implemented on the contaminant plume to prevent impact to the potential receptor. Sentinel well location(s) should be determined based on the groundwater flow direction, velocity, and distance to potential receptors. It should be noted that ground water velocity and flow paths, and therefore, contaminant transport may be influenced by the treatment application (e.g., injections may increase the hydraulic head and alter the assumed groundwater flow path). The sentinel well should be located based on the behavior of the contaminant plume (i.e., stable, shrinking, advancing, or diving) and on ground water monitoring data obtained from the plume monitoring wells and anticipated impacts that may be caused by any injections. As indicated by the Department's Field Sampling Procedures Manual (6.9.2.5.1.10), depth discrete sampling is **not** recommended for sentinel wells with a saturated screen length greater than five feet unless the well is vertically profiled every sampling round. This recommendation is due to the uncertainty regarding the depth at which the contaminant front will arrive in the well.

### Background Wells

Background monitoring wells may include a single monitoring well, or multiple monitoring wells depending upon the size of the source area, and should be located sufficiently upgradient of the source area to be representative of background soil and groundwater conditions at the site. An understanding of groundwater flow direction is important to ensure that the location of the monitoring well(s) is upgradient from the source area. Consideration should be given to the depth of impact in the source area to ensure that the background well(s) monitor the same depth interval(s) affected by the contamination.

If it is not practical to install any upgradient wells, a clean side gradient well may be appropriate for determining ground water quality representative of natural or pre-treatment conditions for secondary parameters that could affect or be affected by the in situ treatment (e.g., pH, dissolved oxygen, iron or other naturally occurring metals, manganese, sulfate).

Background monitoring wells may also be utilized to detect contamination migrating onto the site, and therefore the investigator should give consideration to the surrounding area and the presence of nearby contaminated properties. The presence of contamination migrating onto the site should be understood, as it may have a direct impact on the effectiveness of the in situ remediation, as well as secondary impacts on ground water quality, which may necessitate changes in the remedial design or approach.

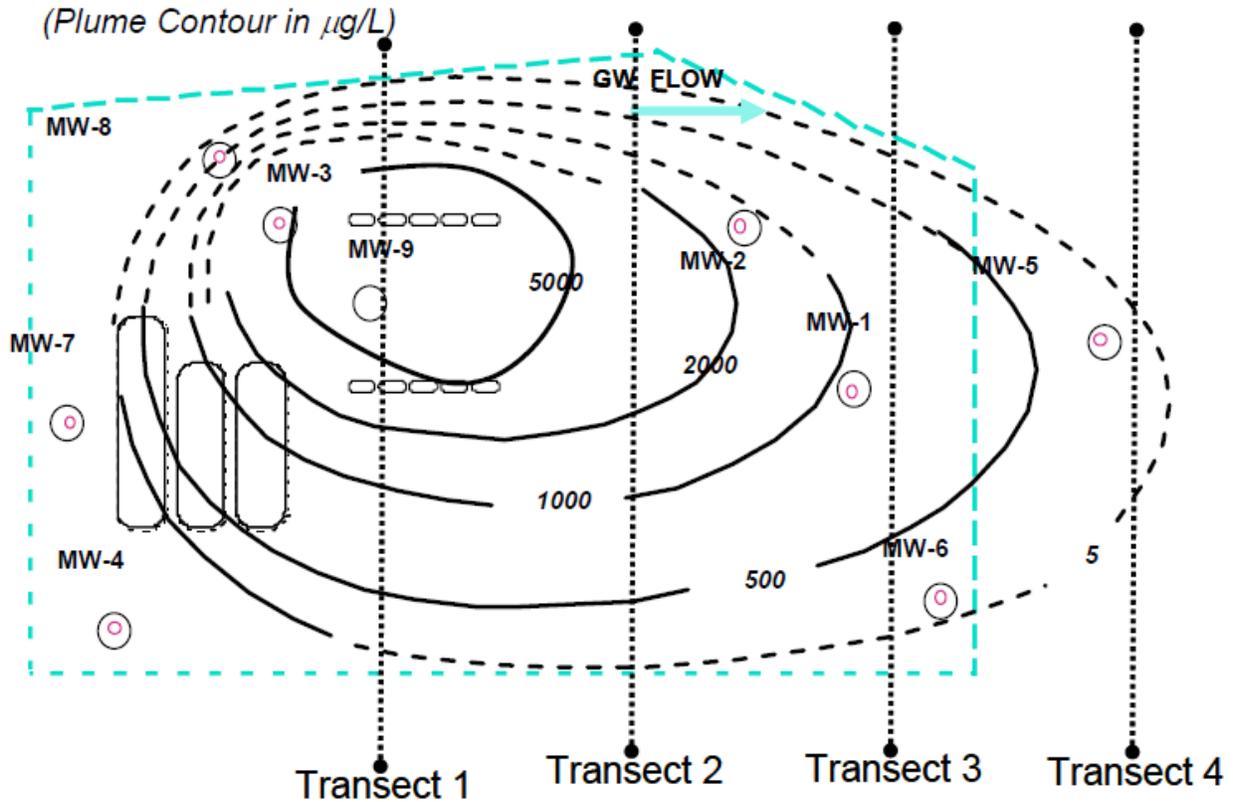


Figure 2. Transects from *Guidance on Remediation of Petroleum-Contaminated Ground Water by Natural Attenuation*, Washington State Department of Ecology, July 2005 (Publication No. 05-09-091 version 1.0)

#### 5.4.1.1. TIMING AND FREQUENCY OF SAMPLING

The timing of sampling in a performance monitoring plan is critical to evaluate the effectiveness of the remediation and to ensure there are no impacts to receptors. Sampling should occur prior to, during, and following treatment application.

Baseline conditions should be established prior to the initiation of remediation either by using historic ground water quality data and/or by conducting one or more separate baseline ground

water sampling events. Data should be representative of source-area, plume-area, and sentinel monitoring wells. If a separate baseline ground water sampling event is performed, it should be conducted to allow sufficient time for the results to be evaluated prior to the initiation of remediation.

Upon commencement of a remedial action, sampling events should be completed at intervals that provide sufficient data to confirm whether the remedial objectives are being achieved and that unintended migration of contaminants or injected material is not occurring. Periodic sampling of the source-area and plume-area performance monitoring wells should occur to:

- 1) Monitor the remedial action to determine whether it is performing as planned and if not, whether modifications should occur in order to improve the performance.
- 2) Determine whether the in situ remedial action may cause unintended exceedances of the applicable ground water quality standards at the conclusion of the remediation – and if so, whether modifications to the in situ remedial action are warranted.

Periodic sampling of the down-gradient performance monitoring wells should occur to determine the following:

- 1) if the in situ remedial action is causing a mass flux of contaminants out of the treatment area – and if so, what modifications should occur to address this
- 2) if the in situ remedial action is creating a flux of treatment reagent(s) out of the treatment area at concentrations exceeding applicable ground water quality standards – and if so, what modifications should occur to address this issue
- 3) if all receptors are protected during and after the remedial action

Frequency of the performance monitoring may range from weekly to annually and will be dependent on the technology being applied and the duration of the treatment. For in situ remedial actions with longer durations, the monitoring frequency may change over time. The timing and frequency of the sampling should account for seasonal fluctuations in the ground water table as indicated in sections 2.8.1, 3.1.3.1 and 4.2 of the Department's Ground Water: SI/RI/RA Technical Guidance ([http://www.nj.gov/dep/srp/guidance/#pa\\_si\\_ri\\_gw](http://www.nj.gov/dep/srp/guidance/#pa_si_ri_gw)).

#### **5.4.1.2. ATTAINING GROUND WATER REMEDIATION GOALS**

When determining if remediation goals have been attained throughout a plume the influence of sampling methodology should be a consideration. Although the low flow sampling method may provide a sample representative of ground water conditions near a well, it also is likely to obtain

a sample from a smaller area surrounding a well than the traditional 3 to 5 well volume sampling method. If samples obtained using low flow sampling indicate that remediation goals have been met in all wells, the investigator should, in many situations, conduct at least one round of sampling using the traditional method for all wells where feasible based on well yield. Sampling in this way is especially appropriate where vertical profiling and/or transects across a plume width have never been done and/or in situations where the location of the source of contamination is uncertain or unknown. Experience shows that sample concentrations can sometimes be significantly higher when the traditional method is used. The difference in results may occur because, for example, an area of residual NAPL is far enough from a monitoring well that contamination from the area is not drawn into the well by the low flow method but is captured by the higher purge rate method.

As stated by ITRC (2005), subsurface conditions should be allowed to re-equilibrate prior to verifying that remedial goals have been met. Sufficient sampling is needed to verify that significant contaminant rebound will not occur. Once such sampling is completed, to evaluate whether the in situ ground water remediation has achieved the final remediation standards, a minimum of two uncontaminated ground water samples taken far enough apart to account for seasonal-fluctuations of ground water conditions should be obtained from all source-area, plume-area, down-gradient treatment- fringe-area, and side-gradient treatment-fringe-area performance monitoring wells.

If the interim remedial goal is to reduce contaminant levels significantly and subsequently use MNA to reach the final remediation standards, sufficient sampling should occur to determine if ground quality has essentially returned to conditions that are no longer significantly enhancing natural attenuation. This determination can be made using trends in COC concentrations, the continued presence of reagents or amendments injected or otherwise discharged, and the resulting changes in geochemical parameters from baseline to post treatment levels.

Post treatment sampling should also document whether background or pre-treatment concentrations/levels or numeric standards have been attained for parameters such as pH, iron, manganese, sulfate, sodium, or other constituents that have ground water quality standards and are present in post-remediation samples due to the reagents used to enhance attenuation or cause destruction of COC. See Section 7.1 for information on permit monitoring requirements for secondary impacts on such parameters.

If background contamination is present on-site from off-site sources, additional sampling of background monitoring wells may be warranted. See the Department's Off-Site Source Ground Water Investigation Technical Guidance. The Department has developed Commingled Plume Technical Guidance that may also be of use. Both guidance documents are found at <http://www.nj.gov/dep/srp/guidance/index.html>.

If during the performance monitoring there are unintended exceedances of the applicable ground water quality standards as a result of the discharge approved under a permit-by-rule, it must be

reported to the Department as specified in the discharge approval letter pursuant to N.J.A.C. 7:14A-6.2(a)14; any appropriate mitigation measures must be implemented pursuant to N.J.A.C. 7:14A-6.2(a)7 and 11. In this situation, sampling should continue as discussed in Sections 7.1.2 and 7.1.4, and, if necessary, as discussed in Section 7.3. If exceedances are expected for certain constituents included in or affected by an in situ technology reagent, these constituents should be included in a “permit-related CEA” which is discussed in Sections 7.1.1. and 7.1.3 with regard to the permit-by-rule and in Section 7.3 regarding the RAP application.

#### **5.4.2. PERFORMANCE MONITORING FOR IN SITU SOIL REMEDIATIONS**

For in situ soil remediation, performance monitoring soil samples should be obtained to evaluate the following two general areas and concerns:

- 1) midway between injection wells within the designed injection grid in order to verify that the in situ soil remediation is effectively remediating soil within the treatment area; and
- 2) locations and depth-intervals with the highest concentrations of soil contaminants that were previously identified.

Consideration should be given for lithologic variations throughout the soil profile.

Backfilled boreholes should not be re-entered during subsequent performance monitoring soil sampling events; soil used to backfill the previous boreholes and any soil that may have caved into the boreholes could be incorporated into the subsequent soil samples, which could bias the analytical results. Performance monitoring boreholes should generally not be located closer than 1.5 feet from backfilled soil borings, as borings can deflect from the vertical into adjacent, backfilled boreholes.

Collection of performance monitoring soil samples should be considered during the treatment in order to determine whether the soil remediation is performing according to the Remedial Action Workplan, and if not, whether modification(s) to the soil remediation should occur to improve the performance of the remediation.

The investigator should obtain post-in situ treatment soil samples in order to evaluate whether the remediation has achieved the remedial objectives specified in the Remedial Action Work Plan. Sampling should be conducted consistent with Section 6.3.2 of the Department’s Technical Guidance for Site Investigation of Soil, Remedial Investigation of Soil, and Remedial Action Verification Sampling for Soil ([http://www.nj.gov/dep/srp/guidance/srra/soil\\_inv\\_si\\_ri\\_ra.pdf](http://www.nj.gov/dep/srp/guidance/srra/soil_inv_si_ri_ra.pdf)) and Section 6.7.5 of the Attainment Guidance ([http://www.nj.gov/dep/srp/guidance/srra/attainment\\_compliance.pdf](http://www.nj.gov/dep/srp/guidance/srra/attainment_compliance.pdf))

### 5.4.3. EVALUATING THE NEED FOR VAPOR MONITORING

The performance monitoring plan should address the potential for fugitive emissions and/or vapor intrusion to nearby structures and/or utilities. The risk of vapor intrusion increases with the presence of product or high levels of chlorinated VOCs in ground water or soils. When developing the monitoring plan, the investigator should identify the locations of utilities and structures in the immediate vicinity of the area to be treated and, if appropriate, incorporate vapor monitoring to evaluate any resulting increase in vapor intrusion risk or any associated mitigation measures. Injected fluids and other discharges may displace in situ vapors, or increase their mobility/volatility and the critical distance criteria in the Department's Vapor Intrusion Technical (VIT) Guidance may not be entirely appropriate for determining which structures to monitor. The 100-foot distance discussed in the VIT Guidance was chosen for evaluating typical conditions where long-term vapor diffusion is usually the major driving force for vapor migration and not the relatively more dynamic conditions that may be induced by injections or discharges into the vadose zone or close to the water table.

Vapor monitoring may be warranted prior to, during, and after injections. When selecting a remedial method, special consideration must be taken where preferential pathways and high contaminant concentrations exist to ensure the safety of surrounding areas. The selected remedial action should not in itself cause exposure to receptors (e.g., ozone injection). Mitigation measures such as vapor extraction, subsurface depressurization systems, ventilation of potential indoor air or utility receptors, or evacuation may be necessary in some situations, especially during or for several months after injections.

Vapor screening is typically performed with a photoionization detector (PID), a combustible gas meter (i.e., lower explosive level meter), or a flame ionization detector (FID) or Organic Vapor Monitor. The investigator may also choose to include the collection of soil gas and indoor air samples and have them analyzed by a certified laboratory depending upon the sensitivity and proximity of nearby receptors and the levels or types of contaminants present.

The VIT Guidance should be followed if intrusion of soil vapor into nearby structures is considered a risk during remediation.

Potential monitoring locations include monitoring and/or vapor extraction wells located within the injection area with screened intervals in the unsaturated zone, utility manholes, vaults, and structures (with and without basements). Vapor screening should be performed prior to injections, during start-up, and periodically thereafter, to monitor for vapor intrusion. Based on the results, additional mitigating measures may be warranted.

Aside from vapor intrusion, the investigator may consider monitoring soil vapor to evaluate the effectiveness of the chosen remediation. Parameters such as Carbon Dioxide, Oxygen, and Compounds of Concern (COCs) can be used to provide evidence of chemical oxidation, potential losses of oxygen through the unsaturated zone, fugitive emissions, and losses of oxygen-yielding

reagents. The specific suite of parameters used for monitoring should be based on the site-specific in situ remedial technologies implemented.

#### **5.4.4. EVALUATE POTENTIAL IMPACTS OF REMEDIAL ACTION ON SURFACE WATER/SEDIMENTS**

When evaluating the use of in situ injections as the remedial action, an evaluation of preferential pathways should be conducted to ensure that the injected solution does not migrate into nearby surface water bodies. If a surface water body is identified in the ecological evaluation as being potentially impacted by the site, collection of surface water and sediment samples should be considered prior to the initial injection event to determine if contaminants of concern and/or parameters of the injection material are present. See the Department's Characterization of Contaminated Ground Water Discharge to Surface Water Technical Guidance ([http://www.state.nj.us/dep/srp/guidance/srra/gw\\_discharge\\_to\\_sw\\_tech\\_guidance.pdf](http://www.state.nj.us/dep/srp/guidance/srra/gw_discharge_to_sw_tech_guidance.pdf)).

Where the use of injections can potentially reach a surface water body, professional judgment must be utilized to determine if additional control such as ground water extraction or containment may be necessary. Where applicable, sentinel well sampling, surface water, and/or sediment should be monitored prior to start-up, during injections, and at a frequency determined to be protective and to ensure no detrimental changes in the surface water body are occurring. Frequency of monitoring should be based on factors such as distance to water body, soil permeability, COCs, ground water flow velocity, and the mobility of the injected material. Surface water monitoring may include the following:

- visual inspection to identify the presence of stressed vegetation, sheens, discolored soils, or bubbling along the shoreline
- field measurements such as dissolved oxygen, conductivity, turbidity, pH, ORP, and temperature
- water sample analysis specific to the site's contaminant(s) of concern and injection solution sediment sampling and pore water sampling.

Data collected during the monitoring event should be utilized to evaluate if any reagent or contaminant migration caused by the injection is reaching the surface water body and if so whether mitigation is warranted. Characterization methods and tools in the Department's Characterization of Contaminated Ground Water Discharge to Surface Water Technical Guidance (<http://www.nj.gov/dep/srp/guidance/index.html>) should be utilized in developing an appropriate monitoring plan for this potential receptor.

#### **5.4.5. EVALUATING POTENTIAL IMPACTS OF REMEDIAL ACTION ON POTABLE WELLS**

When developing a monitoring plan for the use of in situ injections or other in situ treatment in the vicinity of potable wells or in an area where future use of ground water as a source of drinking water is likely, the investigator should evaluate if the treatment could have a significant

negative impact on any current or future underground sources of drinking water. If there is a high risk of impacting underground sources of drinking water, injections may not be a viable option.

When utilizing in situ treatment, consider impacts from both hazardous substances and constituents with secondary drinking water standards such as sodium, sulfate, iron and pH. In some situations, it may be appropriate to mitigate secondary impacts of non-hazardous substances in some remediation products. For example, this could be accomplished through pH buffering, flushing with clean water to dilute the concentrations of constituents such as sodium and sulfate in ground water, or other similar approaches to prevent or minimize impacts to underground sources of drinking water.

If it is determined that injection technology can be utilized with minimal risk of impacting the potable wells, potable water samples should be collected as follows:

- 1) prior to initiation of remediation
- 2) during remediation at a frequency based on factors such as distance to potable wells and their screened/open hole depth intervals, groundwater flow velocity, pumping rates, zone of influence, and seasonal fluctuations in groundwater usage.

Monitoring parameters should include site contaminants of concern and any constituents included in, or impacted by, the reagents injected or substances otherwise discharged. They should also include any naturally occurring constituents that may be solubilized or mobilized as a secondary impact of a remedial technology (i.e., pH, iron, manganese, arsenic).

The investigator is reminded that when evaluating the risk of impact to a well, it is not just the well depth that should be considered, but the top of the well screen or open hole interval, as well as usage yield.

## **6. TECHNOLOGY SPECIFIC PERFORMANCE MONITORING**

This section of the technical guidance includes an overview of several in situ remedial technologies followed by three more sections with specific performance monitoring guidance for selected in situ remedial technologies. The technology specific sections include brief descriptions of the technologies and, as needed, performance monitoring goals/objectives, conditions that support the application of the technologies, guidance on monitoring networks, sampling frequency and duration, and the recommended performance monitoring parameters.

Each section is followed by a detailed monitoring parameter table. See Tables 1, 2, 5, 6, 7, and 8. Each table lists parameters that are standard or required (Note \* or 1), recommended (Note 2), or conditionally recommended (Note 3) for the technologies discussed in that section. See Section 5.4 for a detailed discussion of Notes 1, 2, and 3.

Parameters with approved testing methods for which laboratory certification is currently offered are contained in PART III (<http://www.nj.gov/dep/enforcement/oqa/docs/part3.pdf>) of the Department's application for laboratory certification. The Department's Office of Quality Assurance (OQA) provides additional information on laboratory certification programs at <http://www.nj.gov/dep/enforcement/oqa/labcert.html>.

For many in situ remediation technologies, a common performance monitoring objective is to determine when and where monitoring data document that the technology has remediated the site to the extent that remaining contaminant levels can be addressed by MNA. While MNA guidance is not included in this document, many of the technologies discussed involve enhancement of the variety of natural abiotic and biotic processes that bring about contaminant attenuation. As stated by the Department's Monitored Natural Attenuation Technical Guidance, MNA becomes appropriate as a sole groundwater remedy when no source is present and site conditions indicate that MNA alone can meet the remediation goals (i.e., GWQS). Refer to the Department's Monitored Natural Attenuation Technical Guidance ([http://www.nj.gov/dep/srp/guidance/#mon\\_nat\\_atten](http://www.nj.gov/dep/srp/guidance/#mon_nat_atten)) on the applicability and detailed performance monitoring requirements for MNA.

At most contaminated sites, two types of performance monitoring are conducted: i.) process performance monitoring; and ii.) remedial effectiveness performance monitoring (i.e., post treatment monitoring). Process performance monitoring is typically completed during the active phase of implementation on a periodic basis to ensure the treatment system is operating as designed. Remedial effectiveness performance monitoring is typically conducted on a less frequent basis after the subsurface has re-equilibrated to pre-discharge conditions. It is primarily to confirm reduction of contaminant mass as per the remedial design objective.

## **6.1. OVERVIEW OF TECHNOLOGIES**

The in situ remedial technologies discussed in this document apply biological, physical/chemical, and/or thermal processes. Sections 6.2 through 6.4 include more detailed information on selected technologies that utilize one or more of the processes described below.

### **6.1.1. ENHANCED BIOLOGICAL PROCESSES**

Enhanced biological processes include techniques to stimulate aerobic or anaerobic contaminant degradation processes often referred to as biostimulation. In situ aerobic processes include the addition of oxygen or atmospheric air directly to the subsurface or through the discharge of an oxygen-releasing solid or liquid slurry into the subsurface to enhance aerobic microbial degradation. In situ anaerobic biodegradation technologies utilize electron donor or other substrates to stimulate the growth of anaerobic microorganisms that degrade halogenated and non-halogenated organic compounds. Where necessary, and as an enhancement to biostimulation, bioaugmentation is the practice of adding cultured microorganisms into the

subsurface for the purpose of facilitating the degradation of specific soil and ground water contaminants.

### **6.1.2. PHYSICAL/CHEMICAL PROCESSES**

Physical and/or Chemical Processes include in situ chemical oxidation (ISCO), in situ chemical reduction (ISCR), air or oxygen sparging (AS), soil vapor extraction (SVE), surfactant flushing, and containment technologies such as barrier walls, stabilization and solidification.

### **6.1.3. THERMAL PROCESSES**

Thermal remediation processes discussed in this section include electrical resistance heating, thermal conduction heating, and steam extraction technologies, where heat is applied to the subsurface to mobilize contaminants for recovery. In addition, thermal technologies can also significantly enhance biotic and abiotic in situ processes that remediate dissolved plumes (e.g., increased temperature can dramatically increase dissolved organic carbon). In situ vitrification, applies sufficient electrical current to the subsurface to vitrify contaminated soils into a solid glass-like material, immobilizing or destroying the contaminants.

## **6.2. BIOLOGICAL PROCESSES**

Biological processes degrade contaminants in a variety of environments such as soil, sediment, bedrock, ground water, and surface water. These biological transformations are typically caused by the indigenous microorganisms that inhabit these environments. Biodegradation by microorganisms leads to conversion of carbon in the contaminants as its by-products or final inorganic end products through mineralization.

The Department of Defense Strategic Environmental Research and Development Program (SERDP) recently published a report where systematic approach was followed using the relationships between specific biogeochemical parameters and degradation rates to determine the most appropriate bioremediation approach at sites impacted with chlorinated ethenes. The key report deliverable is a decision tool, termed BioPIC, that can be used to estimate and integrate the impact of quantifiable parameters on natural attenuation and microbial remedies to achieve degradation of chlorinated ethenes (ESTCP Project ER-201129, December 2015).

In situ bioremediation is the application of biological treatment technologies to remediate contaminants present in the subsurface soil and ground water. During the process of in situ bioremediation, microorganisms use the organic contaminants as a carbon and energy source for their growth, resulting in contaminant breakdown. In relatively few instances, biodegradation is not linked to direct microbial growth but instead to a process termed co-metabolism. This process is discussed separately. Microorganisms are capable of degrading the contaminants

through a variety of biochemical reactions including dechlorination, hydrolysis, oxidation, reduction, dehydrogenation, dehydrohalogenation, and substitution. Broadly, microorganisms can carry out degradation under aerobic and anaerobic conditions. These two degradation processes are detailed below.

### **6.2.1. ANAEROBIC PROCESSES**

Anaerobic biodegradation occurs in environments deficient of molecular oxygen where microorganisms use alternate electron acceptors such as nitrate, iron, manganese, sulfate, and carbon dioxide for respiration with organic carbon serving as the electron donor source to promote contaminant degradation. Sometimes, microorganisms respire on chlorinated substrates, using them as electron acceptors and causing their breakdown. Degradation using nitrate as an electron acceptor is performed by denitrifying or nitrate-reducing organisms and degradation using iron (ferric) is promoted by iron-reducing bacteria. Degradation using sulfate and other sulfur oxyanions is caused by sulfate-reducing bacteria, while degradation that uses carbon dioxide is catalyzed by methanogenic bacteria. Several in situ remedial technologies are developed to degrade contaminants in the subsurface taking advantage of these anaerobic microbial processes.

#### **6.2.1.1. ENHANCED ANAEROBIC ATTENUATION THROUGH BIOSTIMULATION**

Biostimulation involves delivering nutrients to subsurface environments to enhance the anaerobic degradation of the contaminants. The nutrients primarily consist of organic carbon and iron (electron donors) and nitrate and sulfate (electron acceptors). Thus, enhanced in situ anaerobic biostimulation accelerates naturally occurring biodegradation of contaminants by creating favorable conditions in the soil and ground water through nutrient addition. The selection of nutrient(s) depends on the site-specific conditions and requires knowledge of the ground water biogeochemical parameters and subsurface environment. For example, subsurface environments impacted with chlorinated compounds are typically limited in electron donors requiring organic carbon and iron addition, while environments with petroleum hydrocarbon impacts are limited in electron acceptors requiring nitrate or sulfate addition.

The most studied ground water contaminants for the enhanced anaerobic biostimulation are the chlorinated solvents belonging to ethene, ethane, methane, and propane groups. Other common ground water contaminants addressed through anaerobic biostimulation are chlorinated benzenes, chlorinated phenols, chlorinated pesticides, polychlorinated biphenyls (PCBs), perchlorate, chlorate, nitroaromatic explosives, dissolved metals (e.g., hexavalent chromium), and inorganic contaminants nitrate and sulfate. Chlorinated solvents are degraded through the reductive dechlorination process where chlorine atoms on the molecule are replaced by hydrogen. The hydrogen required is provided through nutrient addition (an organic carbon substrate which ferments and produces hydrogen) or through direct addition as hydrogen and acetate into the subsurface. These additions create an anaerobic environment favorable for chlorinated solvent

degradation. A variety of organic carbon substrates are used in the biostimulation including lactate, emulsified vegetable oil, lecithin, fatty acids, molasses, and alcohols.

Recently, it was reported that the limited bioavailability of corrinoid compounds might limit the ability of bacteria to dechlorinate chlorinated solvents such as TCE. Vitamin B-12 (cyanocobalamin) was reported responsible for the corrinoid production and expression of dechlorination activity. Cultures of *Dehalococcoides* strains grown with limiting amounts of vitamin B-12 expressed poor and incomplete dechlorination compared to cultures that were exposed to the vitamin (Yan et al., 2013). Thus, vitamin B-12, along with organic carbon electron donor sources, are important to stimulate dechlorination activity. While some aquifers may already be anaerobic, biostimulation may be required to enhance degradation rates. Several anaerobic biostimulation studies have been conducted to date resulting in reliable data collection allowing better biostimulation remedial designs in the future.

#### **6.2.1.1.1. ANAEROBIC BIOSTIMULATION APPLICATION, NETWORK WELLS, AND SAMPLING**

Typical anaerobic biostimulation system configurations include: (i) source treatment where remediation of source zones is addressed through substrate/contaminant contact; (ii) plume containment where remediation is addressed using a biologically reactive barrier to reduce mass flux from a source zone or across a specified boundary; and (iii) plume-wide restoration where remediation of an entire dissolved plume is addressed. In some cases, several approaches may be combined such as targeting a source area in combination with a linear barrier configuration close to the down gradient edge of the plume. In general, site-specific remedial objectives of biostimulation are often either to reduce contaminant levels enough to allow for natural attenuation of remaining levels or to fully restore contaminated ground water to the applicable remediation standards, and or site goals/objectives. If exposure pathways such as surface water discharge or volatilization to soil vapor are the major considerations at a site, they are likely to dictate remedy design.

Performance monitoring wells should be located upgradient, within, and downgradient of the biostimulation zone, parallel to the direction of ground water flow. These wells are intended to monitor changing ground water chemistry over time along the ground water flow path through the biostimulation treatment area. It may be beneficial to have at least one monitoring location within the injection area screened at multiple depths to determine vertical hydraulic gradients, the potential for vertical migration of substrate, and the vertical extent of the treatment zone. Cross-gradient well locations may also be useful to define the lateral extent of treatment.

Performance monitoring is typically conducted on a quarterly to annual basis for most biostimulation systems. In some instances, longer-term performance monitoring may be tied to annual site-wide monitoring programs. For slow-release substrates (such as emulsified vegetable oil, chitin, and polylactate ester) where there is no significant operation and maintenance component, quarterly to semiannual monitoring is sufficient initially. Typical lag times to

stimulate measurable increases in the rate of degradation of chlorinated ethenes may be on the order of months. In these cases, frequent sampling for contaminants being treated, on the order of weeks to a month, may result in an unjustified lack of confidence in the effectiveness of the system.

#### **6.2.1.1.2. ANAEROBIC BIOSTIMULATION PERFORMANCE MONITORING**

The performance monitoring of anaerobic biostimulation consists of the analysis of parameters that will measure the effect of biostimulation in terms of whether defined remedial objectives, compliance numbers, or operational end points have been achieved. Some suggested performance monitoring parameters and metrics that may be applicable are listed below:

- Compare concentrations of parent chlorinated compounds to those of their dechlorination products (such as *cis*-1,2-dichloroethene (*cis*-1,2-DCE), vinyl chloride (VC), and ethene where perchloroethene (PCE) and trichloroethene (TCE) are the parent compounds) to determine extent of dechlorination, stalling, and mineralization.
- Measure total organic carbon (TOC) and volatile fatty acids (VFAs) to determine electron donor longevity.

Electron donors are primarily made up of organic carbon and are required for dechlorination. VFAs include lactic acid, acetic acid, pyruvic acid, propionic acid, and butyric acid; their presence confirms the fermentation of slow release organic carbon substrates emulsified vegetable oil and lecithin.

- Ground water geochemistry measurements in terms of microbial respiratory substrates and products (pH, DO, ORP, hydrogen sulfide, alkalinity, nitrate, iron, sulfate, and dissolved methane).

The pH of ground water is an important parameter for the expression of dechlorination activity; the optimal range is 6 to 8 s.u. The geochemistry data provides information on the type of microbial process involved in contaminant degradation.

- Confirm that the effective radius of influence (ROI) is consistent with the designed ROI for the anaerobic biostimulation systems to ensure adequate distribution of electron donors or other injectants.
- If feasible, compare the native and biostimulated degradation rates to measure the effectiveness of added electron donors.
- Identify whether there are any negative impacts to ground water quality (e.g., metals) from injected nutrients or due to unintended displacement of the plume.

- Evaluate any monitoring data from other media for potential impacts to nearby receptors and/or transfer of contaminants and injectants from one medium to another.
- Identify the need for any system modifications by comparing the original design data with the performance monitoring data.
- Consider Compound Specific Isotopic Analysis (CSIA) where degradation of parent compounds is not discernible such as degradation of PCE and TCE without the detection of any by-products or BTEX degradation where by-products are not common.

The primary principle of isotope analysis involves the concept of enrichment, which is a known pattern of fractionation that occurs during certain transformation processes such as biodegradation. For example, when a chlorinated parent compound such as PCE biodegrades it is preferentially depleted of molecules containing the  $^{12}\text{C}$  atom and consequently the remaining PCE becomes enriched in  $^{13}\text{C}$ . The process is depicted in the graphic below (fig. 3), which follows the biodegradation over time (or distance) from left to right. Note too that as the PCE becomes enriched in  $^{13}\text{C}$ , its daughter product TCE becomes enriched in  $^{12}\text{C}$ . Fractionation or enrichment patterns of parent and daughter compounds provide insight into the evolution of contaminant plumes as they migrate away from their source areas. They can also help determine if one or more sources are contributing to the presence of a contaminant at a given location.

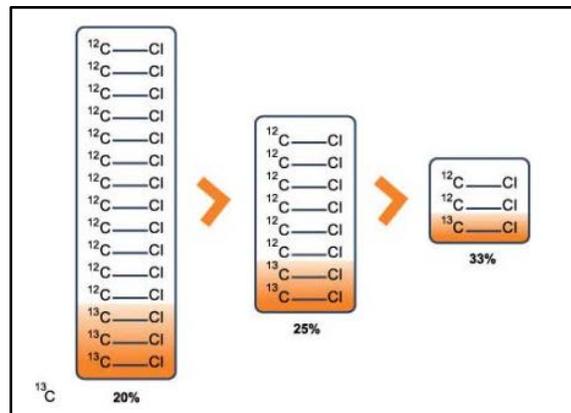


Figure 3. Biodegradation of PCE

Source: EPA 600/R-08/148, *A Guide for Assessing Biodegradation and Source Identification of Organic Ground Water Contaminants using Compound Specific Isotope Analysis (CSIA)*, December 2008.

### 6.2.1.2. ENHANCED ANAEROBIC ATTENUATION THROUGH BIOAUGMENTATION

Enhanced anaerobic attenuation through bioaugmentation is a process where naturally-occurring or engineered microorganisms are added along with the biostimulants to degrade the contaminants. The primary reason for selecting bioaugmentation technology is to augment the native bacterial population responsible for degrading the contaminants and shorten the remediation time or delivery of bioaugmented cultures where responsible degradative microorganisms are absent. Anaerobic bioaugmentation is most commonly applied to treat chlorinated aliphatic compounds including chlorinated ethenes (PCE, TCE, cis-DCE, and VC), chlorinated ethanes (1,1,1-trichloroethane and 1,1,2,2-tetrachloroethane), chlorinated methanes (carbon tetrachloride and chloroform) and chlorinated propanes (1,2,3-trichloropropane (TCP) and 1,2-dichloropropane (DCP)).

With respect to chlorinated ethenes remediation, the most accepted form of bioaugmentation involves the use of anaerobic cultures belonging to different *Dehalococcoides* (DHC) strains. Complete sequential dechlorination of PCE to ethene was demonstrated in 1997 (Maymo-Gatell, et al., 1997). Metabolically and phylogenetically distinct subgroups include *Dehalococcoides ethenogenes*, *Dehalococcoides* strain 195, *Dehalococcoides* strain CDBD1 (Pinellas subgroup), *Dehalococcoides* strain BAV1 (Pinellas subgroup), and *Dehalococcoides* strain VS (Victoria subgroup). Different strains of DHC strains may only degrade certain chlorinated aliphatic hydrocarbons (CAHs). In general, microorganisms capable of degrading PCE and TCE to cis-DCE are ubiquitous and bioaugmentation may be most beneficial when there is a low density of *D. ethenogenes*. Often, cis-1,2-DCE and VC, daughter products of TCE, accumulate when dechlorination is incomplete; this is referred to as “cis-DCE stall.” This limited dechlorination is primarily due to lack of DHC bacteria at the site or presence of multiple contaminants groups (e.g., chlorinated ethanes and methanes co-mingled with ethenes). Bioaugmentation has now been successfully demonstrated at full-scale for multiple sites, and commercially available bioaugmentation cultures are widely available from multiple vendors.

With respect to chlorinated ethanes and methanes remediation, microorganisms consisting of DHC strains and *Dehalobacter* (DHB) strains are found to degrade these chlorinated groups through complementary dechlorination activities. Another CAH group of interest is chlorinated propanes. *Dehalogenimonas* (DHG) strains may be responsible for 1,2,3-TCP and 1,2-DCP dechlorination. Bioaugmentation cultures to degrade chlorinated ethanes, methanes, and propanes are also available commercially (Grostern and Edwards, 2006; Grostern et al., 2010).

In addition to CAHs, biodegradation of PCBs has been demonstrated. For example, bioremediation of PCBs through bioaugmentation is feasible by the sequential activity of halorespiring *Dehalobium chlorocoercia* DF1 and aerobic *Burkholderia xenovorans* LB400 (Payne et al., 2013). This is achieved by biocatalytic SediMite™ (an innovative solid substrate that includes activated carbon particles) application where microorganisms are delivered into sediments as pellets to help form microbial biofilms, and sequester and concentrate hydrophobic

PCBs in close proximity to the biofilm of PCB transforming bacteria facilitating the degradation. However, the PCB degradation report by anaerobic bioaugmented cultures are limited and demonstrated in bench scale and pilot scale but not under full scale field conditions.

#### **6.2.1.2.1. ANAEROBIC BIOAUGMENTATION APPLICATION, NETWORK WELLS, AND SAMPLING**

In situ conditions that support anaerobic biostimulation, described in Section 6.2.1.1.1, are also typically applicable to anaerobic bioaugmentation and the guidance provided in that section for well networks and sampling should also be applied to anaerobic bioaugmentation sampling.

#### **6.2.1.2.2. ANAEROBIC BIOAUGMENTATION PERFORMANCE MONITORING**

It is recommended that performance monitoring to measure the effectiveness of anaerobic bioaugmentation include those metrics listed under the anaerobic biostimulation in Section 6.2.1.1.2, as well as the following parameters as applicable:

- Analyze samples for gene-specific microbial analysis (i.e., 16S rDNA) such as DHC to detect DHC-related strains known to degrade chlorinated ethenes; or specific to DHB strains known to degrade chlorinated ethanes and methanes; or specific to DHG strains known to degrade chlorinated propanes.
- Analyze samples for vinyl chloride reductase gene that converts VC to ethene (commonly referred to as VCR and BAV genes).
- Analyze samples for “QuantArray” which provides quantification of important organisms and functional genes responsible for biodegradation of a group of contaminants and therefore more comprehensive site assessment (ITRC 2011 and 2013).

#### **6.2.1.3. PERMEABLE REACTIVE BARRIERS**

Permeable reactive barriers (PRBs) are an in situ treatment technology where the groundwater plume is intercepted and remediated through contact with reactive materials present or injected into the barrier to utilize chemical, physical, and/or biological processes. This section describes PRBs using biological processes. The PRB system is typically operated in hydraulically passive mode (i.e., groundwater and the target chemicals flow through the PRB under natural hydraulic gradients without mechanical assistance). PRB technology is evolving; new and innovative reactive materials are being introduced to treat different contaminants. PRB's can be used to remediate a variety of contaminants using a variety of reactant materials; mulch for treating chlorinated solvents, nitrate, metals, and energetic and munitions compounds; carbon and zero-valent iron (ZVI) and other forms of iron to facilitate biotic and abiotic dechlorination; and zeolites for treating radionuclides and heavy metals. PRB installation methods include the use of single-pass trenchers, large-diameter augers, excavators, and other techniques.

### **6.2.1.3.1. PERMEABLE REACTIVE BARRIER APPLICATION, NETWORK WELLS, AND SAMPLING**

The primary use of a PRB is to eliminate or substantially reduce the mass discharge of the contaminant(s) downgradient of the PRB. It may be used near the source area, or it may be installed farther down-gradient to protect receptors. The treatment of contaminated groundwater occurs within the PRB or within a relatively short distance from the downgradient edge of the PRB, depending on the specific PRB design. For example, the release of hydrogen or organic carbon from an iron-based or mulch-based PRB may enhance biodegradation processes a short distance downgradient from the PRB.

Performance monitoring wells should be located upgradient, within, and downgradient of the barrier, parallel to the direction of groundwater flow. The monitoring wells should be located immediately or close to PRB and preferably in a transect. Location of downgradient monitoring wells at a greater distance away from the PRB will likely measure contaminant concentrations due to back diffusion in that vicinity rather than measuring the actual PRB performance. These wells are intended to monitor changing groundwater chemistry over time along the groundwater flow path through the PRB treatment area. Consideration should be given to the groundwater seepage velocity and the desired frequency of performance monitoring when determining monitoring locations and spacing. In general, monitoring well screen intervals should be similar to the injection interval(s). For PRBs containing slow-release substrates where there are no significant operation and maintenance activities, quarterly to semiannual monitoring may be sufficient for the initial sampling phase. In contrast, more frequent sampling may be necessary during the initial sampling phase for PRBs containing reactive materials consisting of a combination of iron along with slow release organic carbon (Ramanand et al., 2014). For example, when iron is added to chemically precipitate high sulfide concentrations formed from biological sulfate reduction, frequent sampling may help evaluate the biological and chemical performance of the PRB.

Vertical monitoring may be necessary to ensure that contaminants do not bypass the PRB.

### **6.2.1.3.2. PERMEABLE REACTIVE BARRIER PERFORMANCE MONITORING**

Performance monitoring to measure the effectiveness of a PRB will depend on the site remediation objective. PRB performance monitoring may include evaluation of the following metrics:

- Provide proper hydraulic control whereby target contaminants are directed through the reactive materials within the PRB with an appropriate residence time and not deflected around, over, or under the PRB without being treated. Groundwater flow nets may be useful in this evaluation.

- Regularly monitor water levels and evaluate hydraulic gradient information to determine the most probable contaminant migration direction and travel rate.
- Perform a combination of water level monitoring and single-hole borehole dilution tests within the PRB at regular intervals (3–5 years) after construction, to ensure the PRB matrix has not become fouled or depleted.
- Measure contaminant treatment *in-situ* to confirm contaminant concentrations are reduced in ground water flowing through the PRB. Analyze for parent chlorinated compounds and their degradation products (such as *cis*-DCE, VC, and ethene where PCE and TCE as the parent compounds) to determine the extent of dechlorination, stalling, and mineralization.
- Determine the downgradient extent of PRB influence.
- Meet specific water quality objectives for target chemicals, including secondary targets: regularly monitor performance and compliance wells per regulatory requirements (typically quarterly to annually).
- Measure groundwater geochemistry in terms of microbial respiratory substrates and by-products (e.g., pH, DO, ORP, alkalinity, nitrate, iron, sulfate, and dissolved methane).
- Evaluate the processes involved in in-situ biogeochemical transformation (ISBGT) that result in biotic and abiotic dechlorination of chlorinated solvents. As part of the ISBGT evaluation, soil (solid) samples should be analyzed for the acid extractable sulfide, chromium reducible sulfides, and weak acid soluble total and ferrous iron.
- As part of long-term monitoring, if the downgradient contaminant results are not consistent with expectations, core samples of the reactive material may be taken to evaluate the reactivity, consistency, and heterogeneity of the barrier. If the differences in static water levels are not consistent with expectations or if there is a shift in hydraulic gradient or preferential pathways are noted, then additional assessment may be warranted. Long term monitoring may also involve assessing the depletion of the reactive material and the need for its rejuvenation; measure for reactive material ingredients such as TOC and ferrous and ferric iron.

#### **6.2.1.4. ANAEROBIC COMETABOLISM**

In anaerobic cometabolism, contaminants are fortuitously degraded by an enzyme or cofactor during the microbial consumption of an alternate carbon source or co-substrate (i.e., microorganisms fortuitously degrade contaminants while reducing other compounds for energy and carbon). Methanol, glucose, acetate, lactate, sulfate, nitrate or pyruvate can serve as co-substrates during the cometabolic anaerobic reduction. The enzymes or cofactors produced in

response to microbial degradation of these co-substrates help degrade the contaminants. There appears to be no energy or growth benefit to the microorganisms during this co-metabolic process.

The most widely studied contaminant where degradation follows the anaerobic cometabolism process is carbon tetrachloride (CT). CT has been shown to degrade under reducing conditions via two major cometabolic pathways: (1) the cometabolic reductive dechlorination pathway where CT is reduced by hydrogenolytic dechlorination reaction producing degradation by-products as would be seen during the direct anaerobic reductive dechlorination (where CT is degraded to chloroform, dichloromethane, chloromethane and ultimately methane); and (2) the cometabolic denitrification pathway where CT degradation results in little to no production of chloroform; however, the mechanisms of this degradation process are not as well understood as reductive dechlorination. Fortuitous metabolism of CT by enzymes produced by denitrifying bacteria results in break down to carbon dioxide without also producing chloroform (ITRC 2002).

Typically, during the cometabolic denitrification process where CT degradation is facilitated, nitrate serves as an electron acceptor. Nitrate is a groundwater contaminant at higher concentrations (greater than 10 mg/L). Thus, cometabolism denitrification favors the degradation of both contaminants (CT and nitrate) wherein organic carbon added to serve as an electron donor will create an environment for microorganisms to use nitrate as a respiratory substrate causing fortuitous degradation of CT.

#### **6.2.1.4.1. ANAEROBIC COMETABOLISM APPLICATION, NETWORK WELLS, AND SAMPLING**

As discussed in Section 5.5 Performance Monitoring Plan, a typical scenario consists of performance monitoring wells in up-gradient and near-source areas, along longitudinal and transverse axes, and at fringe/sentinel well areas. In simple cases, an array consisting of an upgradient, source, and downgradient plume fringe/sentinel wells may suffice.

#### **6.2.1.4.2. ANAEROBIC COMETABOLISM PERFORMANCE MONITORING**

Suggested cometabolism performance monitoring analytical parameters and metrics that may be applicable are listed below:

- Compare concentrations of contaminants to those of their degradation by-products to determine extent of dechlorination and mineralization.

For example, a decrease in the concentration of contaminants such as CT and transient formation of its by-products such as chloroform, dichloromethane, and chloromethane (methylene chloride) is indicative of bioremediation.

- Analyze TOC to determine electron donor longevity; electron donors are primarily made up of organic carbon and are required for dechlorination.
- Analyze nitrate/nitrite, as a decrease in concentration of this electron acceptor may indicate active bioremediation.
- Analyze alkalinity, as an increase over background is indicative of microbial respiration and biodegradation.
- Evaluate DO and ORP data - DO concentration of 2 mg/L or less and ORP of around 750 mV support denitrifying conditions.
- Analyze for sulfate as this concentration, along with contaminant by-products data, will provide evidence for type of metabolic pathway for contaminant degradation.
- Ensure nutrients (nitrogen and phosphorous) required for the microbial metabolism is present in adequate amounts.
- Analyze dissolved methane as its presence will indicate highly reduced groundwater conditions typically not favoring CT or nitrate degradation.

Table 1. Performance monitoring parameters for bio-anaerobic technologies

| Sampling Media / Parameters                          | Anaerobic Biostimulation / Bioaugmentation | Permeable Reactive Biobarrier |                       |                               | Anaerobic Co-metabolism |
|--|--|-------------------------------|-----------------------|-------------------------------|-------------------------|
|  |  | Organic Carbon                | Organic Carbon / Iron | Organic Carbon / Sulfate/Iron |                         |
| <b>Field Parameters<sup>+</sup></b>                  |  |                               |                       |                               |                         |
| pH*  | *  | *                             | *                     | *                             | *                       |
| Dissolved oxygen*                                    | *  | *                             | *                     | *                             | *                       |
| Oxidation-reduction potential*                       | *  | *                             | *                     | *                             | *                       |
| Temperature*   | *  | *                             | *                     | *                             | *                       |
| Conductivity*  | *  | *                             | *                     | *                             | *                       |
| Ferrous iron   | 2  | 2                             | 2                     | 2                             | 2                       |
| Hydrogen Sulfide                                     | 2  | 2                             | 2                     | 2                             | 2                       |
| Depth to water*                                      | *  | *                             | *                     | *                             | *                       |
| Depth of well*                                       | *  | *                             | *                     | *                             | *                       |
| <b>Lab Parameters - Ground Water</b>                 |  |                               |                       |                               |                         |
| Volatile organic compounds (VOCs)                    | 1, 2                                       | 1, 2                          | 1, 2                  | 1, 2                          | 1, 2                    |
| Alkalinity   | 2  | 2                             | 2                     | 2                             | 2                       |
| Nitrate-nitrite nitrogen                             | 2  | 2                             | 2                     | 2                             | 2                       |
| Ammonia nitrogen                                     | 3  | 3                             | 3                     | 3                             | 3                       |
| Total Phosphorus                                     | 3  | 3                             | 3                     | 3                             | 3                       |
| Total iron   | 1, 2                                       | 1, 2                          | 1, 2                  | 1, 2                          | 1, 2                    |
| Dissolved iron                                       | 2  | 2                             | 2                     | 2                             | 2                       |
| Total manganese                                      | 1, 2                                       | 1, 2                          | 1, 2                  | 1, 2                          | 1, 2                    |
| Dissolved manganese                                  | 2  | 2                             | 2                     | 2                             | 2                       |
| Total arsenic  | 2  | 2                             | 2                     | 2                             | 2                       |
| Sulfate  | 1, 2                                       | 1, 2                          | 1, 2                  | 1, 2                          | 1, 2                    |
| Dissolved carbon dioxide                             | 3  | 3                             | 3                     | 3                             | 3                       |
| Dissolved ethene, ethane, and methane                | 2  | 2                             | 2                     | 2                             | 2                       |
| Dissolved acetylene                                  | 4  | 4                             | 3                     | 3                             | 4                       |
| Total organic carbon                                 | 2  | 2                             | 2                     | 2                             | 2                       |
| Volatile fatty acids                                 | 3  | 3                             | 3                     | 3                             | 3                       |
| Chloride   | 1, 2                                       | 1, 2                          | 1, 2                  | 1, 2                          | 1, 2                    |
| Bromide (or other tracer) (a)                        | 3  | 3                             | 3                     | 3                             | 3                       |
| Major cations (b)                                    | 3  | 3                             | 3                     | 3                             | 3                       |
| Molecular biology assays (c)                         | 3  | 3                             | 3                     | 3                             | 3                       |
| Compound specific isotopic analysis                  | 3  | 3                             | 3                     | 3                             | 3                       |
| <b>Lab Parameters - Soil</b>                         |  |                               |                       |                               |                         |
| Contaminants and breakdown products                  | 3  | 3                             | 3                     | 3                             | 3                       |
| Fraction organic carbon                              | 3  | 3                             | 3                     | 2                             | 3                       |
| Total iron   | 3  | 3                             | 3                     | 2                             | 3                       |
| Acid volatile sulfide (AVS)                          | 4  | 4                             | 3                     | 2                             | 4                       |
| Chromium extractable sulfide (CES)                   | 4  | 4                             | 4                     | 3                             | 4                       |
| Weak acid soluble ferrous and ferric iron (WAS-Fe)   | 4  | 4                             | 4                     | 3                             | 4                       |
| Strong acid soluble ferrous and ferric iron (SAS-Fe) | 4  | 4                             | 4                     | 3                             | 3                       |
| X-Ray Diffraction                                    | 4  | 4                             | 4                     | 3                             | 4                       |
| Scanning Electron Microscopy                         | 4  | 4                             | 4                     | 3                             | 4                       |

Notes: See Section 5.4 for a detailed discussion of notes 1, 2, and 3 below.

+ - For Field Parameters see Appendix B

\* - Standard field parameters for all ground water sampling events

1 – Required parameter for DGW permits if a COC or related to a direct or indirect impact of DGW.

2 - Recommended analysis.

3 - Conditional analysis.

4 - Analysis not applicable.

(a) Injectant indicators and tracers vary by technology. These may include field colorimetric indicators and/or shake testing (see Appendix B) for soil flushing agents, field and/or laboratory analysis of helium for air sparge helium tracers, laboratory analysis of indicators for soil flushing agents, etc.

(b) Includes calcium, magnesium, sodium, and potassium.

(c) Includes Phospholipid Fatty Acids (PLFA), CENSES, and QuantArray.

## **6.2.2. AEROBIC PROCESS**

The degradation of organic compounds in the presence of oxygen is called aerobic biodegradation. In aerobic biodegradation, microorganisms use molecular oxygen to oxidize part of the carbon in the contaminant to carbon dioxide, with the remainder of the carbon used to produce new microbial cell mass. In this process the oxygen gets reduced, producing water. Thus, the major by-products of aerobic biodegradation are carbon dioxide, water, and an increased microbial population.

### **6.2.2.1. BIOVENTING**

In situ bioventing technology uses microorganisms to degrade organic constituents adsorbed on soils in the unsaturated zone by inducing air or oxygen flow into the unsaturated zone. Typically, oxygen is delivered to subsurface wells at airflow rates sufficient to provide only enough oxygen to sustain microbial activity and not to cause volatilization or stripping of the contaminants. The advantage of bioventing is that it speeds the contaminant degradation process, since oxygen is most often the factor that limits the efficiency of microbial degradation. Air Force Center for Environmental Excellence (AFCEE) in 1992 developed a protocol titled “Test Plan and Technical Protocol for a Field Treatability Test for Bioventing” to primarily remediate JP-4 impacted soil (AFCEE, December 1992). The elements involved in bioventing are detailed below.

The air is delivered to the unsaturated zone employing either of two methods – through injection or extraction. Injection systems are simpler and less expensive to install and operate because they require no treatment of off-gases (compared to an extraction system where contaminants may be pulled to the surface that may require treatment). Injection systems are favored at sites with low-permeability soils and with contaminants of low vapor pressure, located relatively deep in the soil. A beneficial side-effect of air injection is its potential to temporarily depress the water table, allowing for treatment of soil in the capillary fringe. The extraction delivery method, on the other hand, can cause the water table to rise slightly, decreasing the volume of contaminated soil that can be effectively treated.

Extraction systems may be preferable for safety reasons, when there is concern of pushing hazardous vapors into buildings or where the contaminant source is in close proximity to a receptor or property boundary (USEPA, 1995).

Typically, an in situ respiration test is conducted to assess the native biodegradation rates at a given site. This test consists of placing an injection well and one or more soil gas monitoring points in the contaminated area at various distances from the injection well, and measuring concentrations of carbon dioxide and oxygen in the soil gas at the monitoring points. Then the injection point is used to vent the soils with air (oxygen) containing an inert ‘tracer’ gas (typically helium) for about 24 hours, with measurements taken at the monitoring points at frequent intervals. The relative concentrations of carbon dioxide, oxygen, and helium are indicators of oxygen consumption which is, in turn, an indicator of the extent of biodegradation. Another design parameter of bioventing is the determination of radius of influence of oxygen distribution. This is defined as the radius to which oxygen must be supplied from an injection location in order to sustain maximal biodegradation. The radius of influence determination will help in designing the number of air injection points to address contamination at the targeted vadose soil area.

#### **6.2.2.1.1. BIOVENTING APPLICATION**

Bioventing is primarily applied to degrade contaminants in the vadose zone soil. The contaminants mostly consist of petroleum hydrocarbons of low molecular weight. However, reports exist on degradation of high molecular weight polycyclic aromatic compounds (PAHs) including pyrene, fluoranthene, and benzo(a)anthracene. Another group of contaminants reported to degrade through bioventing is chlorinated aliphatics (such as 1,2-DCA and TCE) and aromatic (such as dichlorobenzenes) compounds. Aerobic biodegradation of many chlorinated compounds may require the presence of a cometabolite (such as toluene). Bioventing has also been applied to remediate unsaturated soils contaminated with certain pesticides and wood preservatives. (USEPA, 1995)

#### **6.2.2.1.2. BIOVENTING PERFORMANCE MONITORING**

Performance monitoring will allow the investigator to assess bioventing system performance, optimize the design parameters (generally adjusting the air flow rate), determine the treatment duration, and evaluate final results.

An important performance monitoring parameter is the determination of contaminant degradation rates, which will enhance the design of the treatment system. To determine this, monitoring points may be installed at appropriate distances from the air injection point(s) to facilitate soil gas sampling and to evaluate bioventing performance. It is recommended soil gas samples for hydrocarbons, oxygen, and carbon dioxide analysis be collected weekly until the test location becomes fully aerated. Subsequently, it is recommended that these soil gas components be measured semi-annually, preferably in the warmest and coldest months, for the duration of the test, which is determined from the data collected. These data should be compared with the atmospheric air and uncontaminated background soils to help measure the progress of biodegradation. Such comparison will provide biodegradation progress which will serve as an

indicator for site closure, which, for petroleum products is on the order of years. When the respiration rate (oxygen uptake) is similar to that of the uncontaminated soils, the site is likely remediated, and final soil samples can be taken to determine residual contaminant concentrations, if any, and results can be compared to the remediation goals.

#### **6.2.2.2. BIOSPARGING**

Biosparging technology uses indigenous microorganisms to degrade organic constituents in the saturated zone. In biosparging, air (or oxygen) and nutrients (if needed) are injected into the groundwater to increase native biological activity. The biosparging process is similar to air sparging except that biosparging primarily promotes biodegradation of constituents rather than volatilization, the primary function of air sparging. Biosparging is used to reduce contaminants concentrations dissolved in groundwater, adsorbed to soil below the water table, and within the capillary fringe. When volatile constituents are present, biosparging is often combined with soil vapor extraction (SVE) or bioventing. The effectiveness of biosparging depends primarily on two factors: (i) the permeability of soil which determines the rate at which oxygen can be supplied to microorganisms in the subsurface, and (ii) the biodegradability of the petroleum constituents which determines both the rate and the degree to which the constituents will be degraded by microorganisms.

The goals of a biosparging system are to configure the biosparging wells and monitoring points in such a way that the (i) sparging wells result in maximum removal of groundwater contaminants and (ii) monitoring wells provide information on the performance efficiency of the remediation system. The placement and number of biosparging points required to aerate the dissolved phase plume is determined primarily by the permeability of saturated soil. The bubble radius (analogous to the radius of influence for air sparging system) is defined as the greatest distance from a sparging well at which sufficient sparge pressure and airflow can be induced to enhance the biodegradation of contaminants. The bubble radius will determine the number and spacing of the biosparging wells. Generally, the bubble radius can range from 5 feet for fine-grained soils to 100 feet for coarse-grained soils. In the biosparging remedy, the rate of biodegradation will depend, in part, on the supply of oxygen to the contaminated area, because aerobic metabolism is much faster than anaerobic metabolism. Laboratory or field pilot test data could be used to estimate the rate of oxygen delivery for sustaining maximum biodegradation.

##### **6.2.2.2.1. BIOSPARGING APPLICATION**

Biosparging is effective in reducing the impacts of petroleum discharges which are predominantly located at underground storage tank (UST) sites. This technology is most often used at sites with mid-weight petroleum products (i.e., diesel fuel, jet fuel) rather than lighter petroleum products (i.e., gasoline) which tend to volatilize readily and are more suitable for removal through air sparging. Biosparging is used for heavier petroleum products as well (e.g., lubricating oils), but these constituents take longer to biodegrade. However, biosparging is not

recommended (i) where free product may be present, to avoid spreading the product, (ii) near structures (e.g., basements, sewers, or other subsurface confined spaces) to prevent impacts, unless a vapor extraction system is in place to control vapor migration; and (iii) where contaminated groundwater is located in a confined aquifer system, as the injected air would be trapped by the saturated confining layer and may not escape to the unsaturated zone (USEPA 1994; Waudby et al., 2004).

#### **6.2.2.2. BIOSPARGING PERFORMANCE MONITORING**

Performance monitoring is necessary to determine if contaminant concentration reduction is occurring in the saturated zone and to ensure remediation is proceeding at a reasonable pace. A variety of methods can be used to measure the remedial performance. One method includes monitoring contaminant levels in the groundwater of the monitoring wells, and if vapor extraction is used, vapor analysis of the vapor probes, well heads, and/or blower exhaust. The groundwater and vapor concentrations are then plotted against time for trend analysis. If asymptotic behavior is persistent for periods of about six months or greater and there is little concentration rebound following periods of temporary system shutdown, the continued performance of the biosparging system should be evaluated to determine whether remedial goals/objectives have been reached. If the remedial goal is further contaminant reduction, then another remedial technology will need to be considered.

Other groundwater factors that affect the efficacy of biosparging are those that affect the growth of the contaminant-degrading microorganisms. These factors that directly influence the microorganisms, and indirectly the biosparging system, include pH, presence of sufficient electron acceptors (dissolved oxygen and others), and nutrient (nitrogen and phosphorus) concentrations. These parameters should be analyzed and correlated to contaminant concentration reduction. Other considerations are the potential for biofouling or plugging of the well screens, which may warrant implementing a well maintenance program.

#### **6.2.2.3. ENHANCED AEROBIC ATTENUATION**

Enhanced aerobic attenuation consists of injection of an oxygen releasing reagent into groundwater to enhance the natural aerobic biodegradation rate of dissolved organic contaminants. Commonly used oxygen releasing reagents include a combination of calcium and magnesium oxyhydroxide, calcium and magnesium hydroxides, and calcium peroxide. These reagents are marketed by several vendors and available commercially. The reagents are introduced to the saturated zone in solid or slurry phases. The calcium and magnesium based reagents, when hydrated by groundwater in the aquifer, are converted to their hydroxides releasing molecular oxygen. The released molecular oxygen serves as a long-term source of electron acceptor for enhancing the natural degradation of dissolved contaminants.

### **6.2.2.3.1. ENHANCED AEROBIC ATTENUATION APPLICATION**

The most studied groundwater contaminants for enhanced aerobic attenuation are the petroleum hydrocarbons group consisting of BTEX, methyl tertiary butyl ether (MTBE), tertiary butyl alcohol, naphthalene, and other polycyclic aromatic hydrocarbons (PAH). These fuel hydrocarbons are degraded through aerobic oxidation where oxygen released by the injected reagents is incorporated into the contaminant resulting in its degradation by microorganisms.

Typical enhanced aerobic attenuation system configurations include: (i) source treatment where remediation of source zones is addressed through reagent/contaminant contact; (ii) plume containment where remediation is addressed using a biologically reactive barrier to reduce mass flux from a source zone or across a specified boundary; and (iii) plume-wide restoration where remediation of entire dissolved plume is addressed. In some cases, several approaches may be combined such as targeting a source area in combination with a linear barrier configuration close to the down gradient edge of the plume.

### **6.2.2.3.2. ENHANCED AEROBIC ATTENUATION PERFORMANCE MONITORING**

As presented in Section 5, it is recommended that performance monitoring wells be located both upgradient, within, and downgradient of the enhanced attenuation zone, parallel to the direction of groundwater flow. These wells are intended to monitor changing groundwater chemistry over time along the groundwater flow path. Consideration should be given to the groundwater seepage velocity when determining monitoring well locations and spacing, in addition to the amount of reagent injected into the aquifer and the potential mounding and migration of the plume. Sampling for performance monitoring is typically conducted on a quarterly basis for most enhanced aerobic attenuation systems.

Performance monitoring should include appropriate sampling and analysis and evaluation that will measure the effect of injected reagent in terms of whether defined remedial objectives or operational end points have been achieved. Suggested performance monitoring analytical parameters and metrics that may be applicable are listed below. Based on site-specific conditions and remedial objectives, additional parameters and metrics may be warranted.

- Analyze and compare concentrations of petroleum hydrocarbon and other contaminants at regular intervals to determine extent of degradation with time.
- Measure of groundwater geochemistry in terms of microbial respiratory substrates and products (pH, DO, ORP, alkalinity, nitrate, iron, sulfate, and dissolved methane). The geochemistry data can indicate the microbial processes that are degrading contaminants.
- If feasible, compare the native and enhanced degradation rates to measure the effectiveness of added reagents.

- Identify whether there are any negative impacts to ground water quality (e.g., metals or nutrients) from injected nutrients or due to unintended displacement of the plume.
- Evaluate any monitoring data from other media for potential impacts to nearby receptors and/or transfer of contaminants and injectants from one medium to another.
- Identify the need for any system modifications by comparing the original design data with the performance monitoring data.
- If appropriate, use environmental molecular diagnostic tools and analyze samples for specific microorganisms or genes coding specific degradation functions. Examples include assays of toluene monooxygenase genes responsible for BTEX degradation, and naphthalene dioxygenase genes responsible for PAH degradation.

Table 2. Performance monitoring parameters for bio-aerobic technologies

| Sampling Media / Parameters                           | Bioventing | Biosparging | Enhanced Aerobic Biodegradation | Aerobic Cometalism |
|---|------------|-------------|---------------------------------|--------------------|
| <b>Field Parameters<sup>+</sup></b>                   |            |             |                                 |                    |
| pH  | *          | *           | *                               | *                  |
| Dissolved oxygen                                      | *          | *           | *                               | *                  |
| Oxidation-reduction potential                         | *          | *           | *                               | *                  |
| Temperature   | *          | *           | *                               | *                  |
| Conductivity  | *          | *           | *                               | *                  |
| Ferrous iron  | 4          | 3           | 3                               | 3                  |
| Depth to water  | *          | *           | *                               | *                  |
| Depth of well   | *          | *           | *                               | *                  |
| <b>Lab Parameters - Ground Water</b>                  |            |             |                                 |                    |
| Volatile organic compounds (VOCs)                     | 1, 2       | 1, 2        | 1, 2                            | 1, 2               |
| Alkalinity  | 4          | 2           | 2                               | 2                  |
| Nitrate-nitrite nitrogen                              | 4          | 2           | 2                               | 2                  |
| Ammonia nitrogen                                      | 4          | 3           | 3                               | 3                  |
| Total Phosphorus                                      | 4          | 3           | 3                               | 3                  |
| Total iron  | 3          | 1, 2        | 1, 2                            | 1, 2               |
| Dissolved iron  | 3          | 3           | 3                               | 3                  |
| Total manganese                                       | 1, 3       | 1, 3        | 1, 3                            | 1, 3               |
| Dissolved manganese                                   | 3          | 3           | 3                               | 3                  |
| Total arsenic   | 2          | 2           | 2                               | 2                  |
| Sulfate   | 3          | 2           | 2                               | 2                  |
| Dissolved carbon dioxide                              | 4          | 3           | 3                               | 3                  |
| Total organic carbon                                  | 4          | 3           | 3                               | 3                  |
| Chloride  | 4          | 1, 3        | 1, 3                            | 1, 3               |
| Bromide (or other tracer) (a)                         | 4          | 3           | 3                               | 3                  |
| Major cations (b)                                     | 4          | 3           | 3                               | 3                  |
| Molecular biology assays (c)                          | 4          | 3           | 3                               | 3                  |
| Compound specific isotopic analysis                   | 4          | 3           | 3                               | 3                  |
| <b>Field Parameters (Soil Gas)<sup>+</sup></b>        |            |             |                                 |                    |
| Soil gas for hydrocarbons, oxygen, and carbon dioxide | 2          | 3           | 4                               | 4                  |
| <b>Lab Parameters - Soil</b>                          |            |             |                                 |                    |
| Contaminants and breakdown products                   | 2          | 3           | 3                               | 3                  |
| Fraction organic carbon                               | 3          | 3           | 3                               | 3                  |
| Total iron  | 3          | 3           | 4                               | 4                  |

Notes: See Section 5.4 for a detailed discussion of notes 1, 2, and 3 below.

+ - For Field Parameters see Appendix B

\* - Standard field parameters required for all ground water sampling events

1 - DGW Required analysis if a COC or related to a direct or indirect impact of DGW.

2 - Recommended analysis.

3 - Conditional analysis.

4 - Analysis not applicable.

(a) Injectant indicators and tracers vary by technology. These may include field colorimetric indicators and/or shake testing (see Appendix B) for soil flushing agents, field and/or laboratory analysis of helium for air sparge helium tracers, laboratory analysis of indicators for soil flushing agents, etc.

(b) Includes calcium, magnesium, sodium, and potassium.

(c) Includes Phospholipid Fatty Acids (PLFA), CENSES, and QuantArray.

### **6.3. PHYSICAL /CHEMICAL PROCESSES**

Physical processes employ injection and/or extraction techniques to displace and remove contaminants from various subsurface environmental media. Physical processes may also employ injection and/or mixing techniques to immobilize contaminants in situ to prevent migration and contact with receptors. Commonly applied in situ physical processes include solidification/stabilization, soil vapor extraction (SVE), air sparging (AS), soil flushing and ground water pumping. Performance monitoring considerations for these physical processes are detailed in Sections 6.3.1 through 6.3.4 below.

Chemical processes typically employ injection techniques to deliver chemicals capable of reacting with and degrading contaminants into innocuous substances. The chemical reactions may be oxidation or reduction. Commonly utilized chemical oxidants are permanganate, persulfate, peroxide and ozone. A commonly used chemical reductant is zero valent iron (ZVI), though other reducing agents are available, some of which are often combined with ZVI. The selection of specific chemical injectants is not only dependent upon the target contaminants, but also site geology, ground water / soil chemistry, and infrastructure / receptors. Performance monitoring considerations for various chemical processes are detailed in Sections 6.3.5 and 6.3.6 below.

In many cases, multiple physical and/or chemical techniques are combined simultaneously and/or sequentially to maximize the efficiency and effectiveness of site remediation. As an example, air sparging may be used simultaneously with peroxide and ozone injection in order to enhance the distribution of the chemical oxidants throughout the target treatment area, while SVE is conducted to capture off-gasses resulting from the air sparging, as well as the chemical reactions of peroxide, ozone and the target contaminants. Further, in cases where non-aqueous phase liquid (NAPL) is present, the SVE/AS/chemical oxidation approach outlined above may be preceded by soil flushing with surfactant and ground water pumping to more cost-effectively remove NAPL from the target treatment area by reducing the demand for costlier chemical oxidants and reducing the SVE off-gas treatment costs. While there are many beneficial synergies when multiple techniques are combined, the investigator must also consider and account for potential negative synergies. Performance monitoring considerations for all the processes applied should be incorporated into the overall performance monitoring plan in the RAW and/or DGW proposal.

#### **6.3.1. SOLIDIFICATION / STABILIZATION**

The objective of solidification/stabilization is to minimize the mobility of the contaminants and to isolate the contaminants from potential exposure pathways. This is commonly done by injecting or mixing the impacted media (i.e., saturated or unsaturated soils) with a solidification agent (e.g., cement). Once the solidification occurs, the contaminants are effectively encased in the stabilizing material, thereby minimizing or eliminating mass transfer from soil to

groundwater and/or soil vapor. A deed notice with an engineering control for the stabilized material and a soil RAP is required. A Ground Water RAP is necessary if site contaminants in ground water contamination are expected to persist beyond the RAR due date for the site.

#### **6.3.1.1. SOLIDIFICATION / STABILIZATION PROCESS PERFORMANCE MONITORING**

The primary process performance monitoring considerations for solidification / stabilization are 1) ensuring that the solidification agent is evenly distributed throughout the treatment zone so that the treatment zone is fully encased and no unsolidified pockets remain, and 2) ensuring that the injection and/or mixing process does not displace contaminants out of the treatment zone.

The design of the process performance monitoring program will depend on the type of solidification / stabilization technology employed. For shallow treatment zones, such as impacted soils associated with former chemical waste lagoons, the solidification / stabilization is commonly accomplished by physically mixing the soils with the solidification agent using standard excavation/auger mixing equipment. In this situation, assuming that the treatment zone has been clearly defined via the RI process, visual observation, with the associated documentation (i.e., photographs, field notes, etc.), of the excavation / mixing process is often sufficient to document that the remedial design parameters have been achieved.

In situations where solidification / stabilization is conducted below the water table, either by pressure injection or by physical mixing in deeper excavations, it is important to understand that the existing groundwater will be displaced by the solidification agent. The remedial design must take into consideration the fact that local groundwater flow will be permanently altered by the treatment process, and the remedial design should include a monitoring well network which will be capable of monitoring both groundwater elevations and groundwater quality during the solidification/stabilization process.

In situations where the solidification agent is introduced via pressure injection, the remedial design should include estimates of the radius of influence for each injection interval around each injection point. Observation wells should be installed at key points both within and around the treatment zone in order to confirm that the estimated radii of influence are being achieved. Injection pressures and injected volume should be continuously monitored in each injection zone.

#### **6.3.1.2. SOLIDIFICATION / STABILIZATION REMEDIAL EFFECTIVENESS PERFORMANCE MONITORING**

As the objective of solidification / stabilization is to prevent the mass transfer of contaminants from soil into groundwater, the primary considerations for remedial effectiveness performance monitoring are as follows.

- Confirming that the Target Treatment Zone has been Effectively Solidified. Once the solidification/stabilization agent has undergone the proper curing period, the most effective way to confirm that the treatment zone is sufficiently solidified is via the collection of core samples. The need for core sampling as well as the number and spacing of the samples should be identified in the RAW and the associated remedial design documents. Core samples should be submitted to a geotechnical laboratory for compressibility, shear strength, porosity, and permeability testing. The results should be compared to the design specifications provided in the RAW or remedial design document. All core locations should be properly plugged with the same solidification / stabilization agent to ensure integrity of overall treatment zone.
- Confirming that the Contaminants are Effectively Isolated. Toxicity characteristic leaching procedure (TCLP) testing can be used to confirm that the constituents of concern are effectively isolated and that the remedy will be effective in minimizing the potential for mass transfer from soil to groundwater. This leaching procedure could be conducted on core samples collected from each AOC, biased toward the areas and zones which featured the highest contaminant concentrations. The TCLP analytical results can be used to determine if the solidified mass will leach constituents into ground water.
- Groundwater Monitoring. The effectiveness of the solidification / stabilization in providing source control for groundwater contamination should be evaluated by conducting groundwater monitoring. In order to fully evaluate the effect of the remedy on the local groundwater flow pattern, groundwater monitoring should be conducted from locations both below and on all four sides of the treatment zone. If the solidification / stabilization has effectively isolated the source zone, then down-gradient dissolved phase contaminants should attenuate over time. At a minimum, eight quarters of groundwater monitoring should be conducted. The resulting data should be statistically evaluated in order to confirm that concentration trends are stable or declining, that the existing Ground Water RAP and CEA are applicable to the new groundwater flow regime, and that the remedy will result in groundwater quality conditions which are protective of human health, the environment, and all the identified receptors. If these conditions are not met, then additional monitoring and/or remedial actions may be necessary.

### **6.3.2. SOIL FLUSHING**

The objective of soil flushing is to aid in the physical removal of target contaminants from saturated zone soils. Soil flushing is typically accomplished by injecting surfactants and/or cosolvents into the saturated zone to increase the solubility and/or mobility of NAPL entrained in the soil pores for subsequent removal. In some instances, soil flushing may be performed in combination with other in situ remediation techniques, such as chemical oxidation or bioremediation (ITRC 2003, EPA 2006, ITRC 2009). In these instances, recovery of the mobilized material is not the primary objective, rather soil flushing is used to increase the

solubility of the contaminants present to enhance in situ treatment. Soil flushing can also be used to desorb contaminants adsorbed on the soil matrix, though this is less commonly applied. Common methods of contaminant removal following surfactant/cosolvent injection are recovery well pumping or multi-phase extraction. The choice of which surfactant or cosolvent to use is dependent upon the physical and chemical properties of the target contaminants and the soil matrix.

#### **6.3.2.1. SOIL FLUSHING APPLICATION**

Soil flushing is typically performed when free-phase NAPL recovery rates are below the effective limits of skimming pumps, passive skimmers or high vacuum multiphase extraction. In these instances, the surfactant injection and total fluids recovery are often conducted at the same wells exhibiting NAPL. Soil flushing may also be employed when soil and/or ground water samples indicate contaminant concentrations are near or above saturation levels even if no free-phase NAPL is observed in monitoring wells. In this instance it is more common to inject the surfactants on the upgradient edge of the source zone and recover the dissolved phased contaminants using down gradient recovery wells. A surfactant or cosolvent capable of increasing the solubility and/or mobility of the target NAPL is injected into the subsurface and typically left in place for a period of hours to days or longer based on the manufacturer's recommendations and site-specific conditions. Use of surfactants with a coalescence time of less than 24 hours is desirable (NAVFAC 2002), allowing for effective recovery of the mobilized NAPL to occur within 24 hours of reagent injection, thereby limiting the potential for migration of the mobilized NAPL. Subsequently, total fluids recovery (ground water/NAPL) is conducted within the treatment zone to recover the mobilized NAPL and surfactant.

#### **6.3.2.2. SOIL FLUSHING PERFORMANCE MONITORING**

##### **6.3.2.2.1. PROCESS PERFORMANCE MONITORING**

One of the greatest risks associated with soil flushing is unintended contaminant migration. Since the primary objective of this technique is to increase the mobility of contaminants, suitable process performance monitoring during implementation is critical to reduce the likelihood of unintended contaminant migration, such as along preferential pathways. The most critical process performance monitoring parameters are those that can be measured in the field as the injection and recovery are occurring; these include the depth to water, NAPL thickness, volume and concentration of solution injected, volume and concentration of recovered fluids.

The presence of certain surfactants and cosolvents may also be monitored by colorimetric and/or indicator field test kits; these should be considered for use when available. When field kits for monitoring residual surfactant/co-solvent are not available or effective for the chosen injection material, collection and analysis of laboratory-analyzed indicator parameters is recommended

prior to and following each injection/recovery event. The presence of several commonly-used surfactants is indicated by methylene blue active substances (MBAS), Standard Methods 5540C for anionic surfactants, or cobalt thiocyanate active substances (CTAS), Standard Methods 5540D for nonionic surfactants. Since other subsurface constituents may react with the MBAS or CTAS, it is important to obtain a pre-injection baseline analysis.

Performance monitoring wells should be located up gradient, down gradient and side gradient of the injection area. These wells should be screened across the water table in order to monitor for changes in ground water elevation and LNAPL thickness. When DNAPL is known or suspected to be present, performance monitoring wells should not create a conduit for vertical migration. The distance of monitoring wells from the injection area will be dependent on site geology and the volume, rate and pressure of material being injected. Depending on the overall vertical extent of the contaminants, as well as injection well depths, monitoring wells of varying depths may be needed in order to evaluate horizontal and vertical movement of mobilized contaminants.

Process monitoring parameters should be monitored at a frequency that allows the investigator to determine that soil flushing activities have reached, but not exceeded the designed area of influence. Measuring depth to water in the observation wells can be used to determine that the design injection area of influence has been reached, but not exceeded. Placement of monitoring wells relative to injection wells is important to ensure this condition can be monitored during injection events. For example, if the target injection area of influence is 10 feet, then a monitoring well should be located approximately 10 feet from the injection well (s), preferably in the down gradient direction at a minimum. Additionally, another monitoring well should be located at a greater distance down gradient to ensure the injection area of influence is not exceeded (i.e., mounding observed at a well located 15 feet away would be an indicator to reduce the injection volume/pressure). When the injection wells are also used as the recovery wells, the investigator should ensure that the volume recovered following an injection event is greater than or equal to the volume of solution injected; preferably, the recovered volume should be 2 to 3 times greater than the injected volume to allow for the recovery of injected material. When recovery occurs down gradient of the injection area, the target recovery volume should be 2 to 3 times greater than the calculated treatment area pore volume. Regardless, the adequacy of the recovery should be verified by sampling as discussed in the following section.

#### **6.3.2.2.2. REMEDIAL EFFECTIVENESS PERFORMANCE MONITORING**

The primary objective of most soil flushing applications is the removal of contaminants from the subsurface. There are several means of monitoring remedial effectiveness; these include determining the mass or volume of contaminants recovered from the subsurface, analyzing target contaminant concentrations remaining in soil and/or ground water and, in cases where NAPL recovery is the objective, measuring the apparent thickness of NAPL in site monitoring wells or calculating LNAPL transmissivity. Each technique is addressed in greater detail below. It is possible that multiple soil flushing events will be necessary to meet remedial objectives. The

timing and frequency of performance monitoring sampling events will be based not only on the number and frequency of injection events but also on actual field observations during and following each soil flushing event.

a) Determining the mass or volume of contaminants recovered from the subsurface

Determining the mass or volume of target contaminants recovered can be accomplished by collecting one or more samples of the recovered fluid stream and using the contaminant concentration and total volume of solution recovered to calculate the mass of contaminant recovered during each soil flushing event. The results from multiple events can be compared to determine the relative effectiveness of each event. The sum of the results can be compared to estimates of the total contaminant mass in the subsurface to assess the overall effectiveness of the remedial approach for the site.

In cases where NAPL recovery is the primary objective, measuring the volume of NAPL recovered during a soil flushing event is difficult as the surfactants / co-solvents typically utilized during soil flushing promote solubilizing of the NAPL and mixing with ground water. Additionally, the total fluids pumping and/or high vacuum multi-phase extraction used to recover the NAPL / ground water mixture typically results in further mixing / emulsification of the NAPL with ground water. While it is possible to measure the total volume of the NAPL / ground water mixture recovered, it is generally not possible to directly measure the volume of NAPL alone recovered.

One technique that can be used to indirectly estimate the volume of NAPL recovery is to collect multiple samples of the recovered total fluids mixture during each event and allow the sample fluids time to separate and measure the approximate percentages of NAPL and ground water. Separation may take several days to weeks based on the surfactant utilized and the constituents present. If the samples are collected periodically, the percent NAPL per sample can be extrapolated to the recorded total fluids volume recovered for that same time period. This is a rather crude method and the investigator is cautioned about comparing these estimated NAPL recovery volumes to the estimated volume of NAPL present in the subsurface. This technique is most appropriately used to semi-quantitatively estimate the change in NAPL recovery from one soil flushing event to the next. Consider the example depicted below (table 3, event #1 and event #2) where the investigator can conclude that the average volume of NAPL recovered during the second event was approximately 19% less than the volume recovered during the first event.

Table 3. Event # 1 and Event # 2

| <b>Event # 1</b>                            |  |                                  |  |
|---|--|----------------------------------|--|
| Fluid Recovery Event (Hours)                | % NAPL Vol in Sample Jar after 2 Weeks | Total Fluids Vol Recovered (gal) | Calc Vol NAPL Recovered (gal) <sup>1</sup> |
| 1   | 20%                                    | 200                              | 40   |
| 2   | 20%                                    | 100                              | 20   |
| 3   | 15%                                    | 100                              | 15   |
| 4   | 15%                                    | 75                               | 11.25                                      |
| 5   | 10%                                    | 75                               | 7.5  |
| 6   | 5%                                     | 60                               | 3  |
| Total                                       | ---                                    | 610                              | 96.75                                      |
| Average Percent NAPL Recovered <sup>2</sup> |  | 16%                              |  |

| <b>Event # 2</b>                            |  |                                  |  |
|---|--|----------------------------------|--|
| Fluid Recovery Event (Hours)                | % NAPL Vol in Sample Jar after 2 Weeks | Total Fluids Vol Recovered (gal) | Calc Vol NAPL Recovered (gal) <sup>1</sup> |
| 1   | 20%                                    | 200                              | 40   |
| 2   | 15%                                    | 100                              | 15   |
| 3   | 10%                                    | 75                               | 7.5  |
| 4   | 10%                                    | 75                               | 7.5  |
| 5   | 5%                                     | 60                               | 3  |
| 6   | 0%                                     | 70                               | 0  |
| Total                                       | ---                                    | 580                              | 73   |
| Average Percent NAPL Recovered <sup>2</sup> |  | 13%                              |  |

Equations:

1. Calculated Volume NAPL Recovered (gal) =  
% NAPL Volume in Sample Jar after 2 Weeks \* Total Fluids Vol Recovered (gal)

2. Average Percent NAPL Recovered =  $\frac{\text{Calc Vol NAPL Recovered (gal)}}{\text{Total Fluids Vol Recovered (gal)}}$

Subsequently, the change in NAPL volume recovered from one event to the next can be calculated using the following equation:

$$\text{Change in NAPL Volume Recovered} = \frac{\text{Avg \% NAPL Recovered Event 2} - \text{Event 1}}{\text{Avg \% NAPL Recovered Event 1}}$$

$$\text{Change in NAPL Volume Recovered} = \frac{0.13 - 0.16}{0.16} = -19\%$$

The investigator can compare changes in NAPL volume recovered over the course of several events in conjunction with the other event-specific data to assist in optimizing future soil flushing events. For instance, one may consider correlating average percent NAPL recovered to static ground water levels to determine seasonal conditions under which soil flushing is more effective. Whether seasonal high water table or low water table is more effective will be dependent on current site conditions as well as site conditions at the time(s) the NAPL was released as well as the properties of the NAPL and the site-specific geology.

b) Analyzing target contaminant concentrations remaining in soil and/or ground water

The remedial effectiveness of one or more soil flushing events can also be assessed by analyzing the target contaminant concentrations remaining in soil and/or ground water following the event(s). It is important for the investigator to wait a sufficient amount of time following a soil flushing event before collecting samples to allow the contaminant concentrations in soil and ground water to return to equilibrium. Short term increases in dissolved phase contaminant concentrations are expected within the first two weeks following the soil flushing event and prior to dissolved phase

recovery. This is evidence that the soil flushing event was successful in mobilizing sorbed-phase contamination from the soil matrix. The timeframe for conditions to return to equilibrium will be based on site-specific conditions. It is recommended to collect the post-event monitoring samples at the same approximate time interval following each soil flushing event. Subsequently, following multiple soil flushing events, a reduction in dissolved phase contaminant concentrations occurs as the source is depleted.

Due to the relatively lower cost and ease of collecting ground water samples versus soil samples, it is common to collect ground water samples more frequently during a remedial program. However, when the target contaminants have a low solubility in ground water and/or for long-term remediations, the investigator should consider collecting interim soil samples prior to the end of the proposed remedial program.

The investigator is encouraged to graph the post-soil flushing event analytical data to depict the rate of change in ground water and/or soil concentrations over time. This information is used to determine when the effectiveness of the soil flushing events declines, indicating a need to alter or end the remedial program. It is useful to include multiple rounds of data from prior to the commencement of soil flushing to establish baseline trends. Consider the following example data depicted in figure 3, where soil flushing was initiated following the May 2008 semi-annual ground water sampling event, and periodic soil flushing events were conducted until December 2012. Once soil flushing was initiated, the ground water sampling frequency was increased to quarterly. After approximately 3 years of periodic soil flushing events, the target contaminant concentration reduction rate began to decrease (during the period of August 2011 through May 2012). Since the target contaminant concentration reduction rate continued to decrease during the May, August and November 2012 ground water sampling events, soil flushing activities were halted following the November 2012 event. Quarterly ground water sampling was continued to monitor for rebound. Soil data can be graphed and assessed in a similar manner.

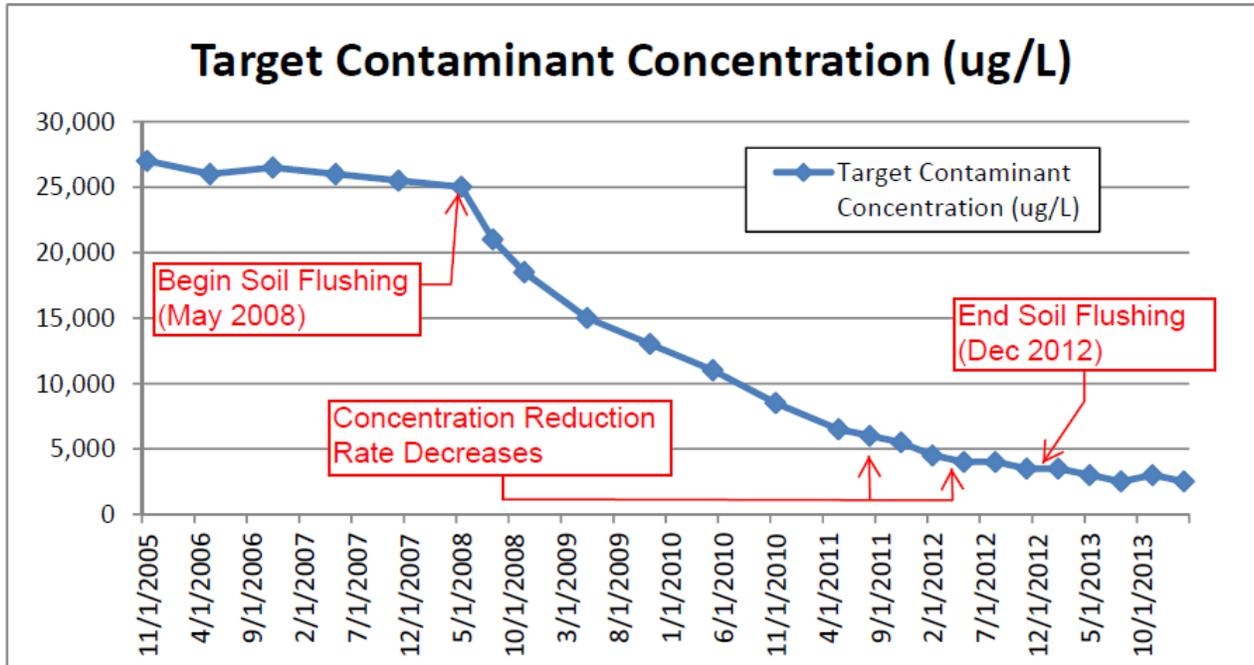


Figure 4. Target contaminant concentration vs. time

c) Measuring the apparent thickness of NAPL in monitoring wells

In cases where NAPL recovery is the primary objective, measuring the NAPL thickness in the target remediation wells will typically be the primary line of evidence to determine the success of the remedial program. While measuring the apparent thickness of NAPL in monitoring wells is straight forward, it may be difficult to determine if a reduction in apparent NAPL thickness from one treatment event to the next is attributable to the treatment event itself and not to water table fluctuations (seasonal, regional dewatering, precipitation events, etc.). This is largely due to the fact that apparent NAPL thickness is often highly dependent on ground water elevations, which may vary seasonally or otherwise at a magnitude that is significant relative to the elevation of NAPL entrained in the soil matrix. It is important to confirm that the elevation of the NAPL layer is below the top of well screen.

One method of data analysis is to overlay a plot of ground water elevation vs time with a plot of apparent NAPL thickness vs time. The data should include measurements collected throughout the year to account for seasonal ground water fluctuations. As such, due to site-specific geologic conditions, it may take 2 to 3 years or more of data to determine if the changes in apparent NAPL thickness are indicative of an overall reduction. This does not necessarily mean that a soil flushing program needs to proceed for multiple years in order to achieve the desired end point of NAPL removal. Regardless of the duration of the soil flushing program, ensure

that there are sufficient representative data points to account for seasonal variations and potential NAPL rebound. As shown in figure 4, the depth to water at the example site was deepest in August relative to the other sampling months. Observed LNAPL thickness was correspondingly greater in August, except in August 2014, signaling the soil flushing program was reaching the endpoint.

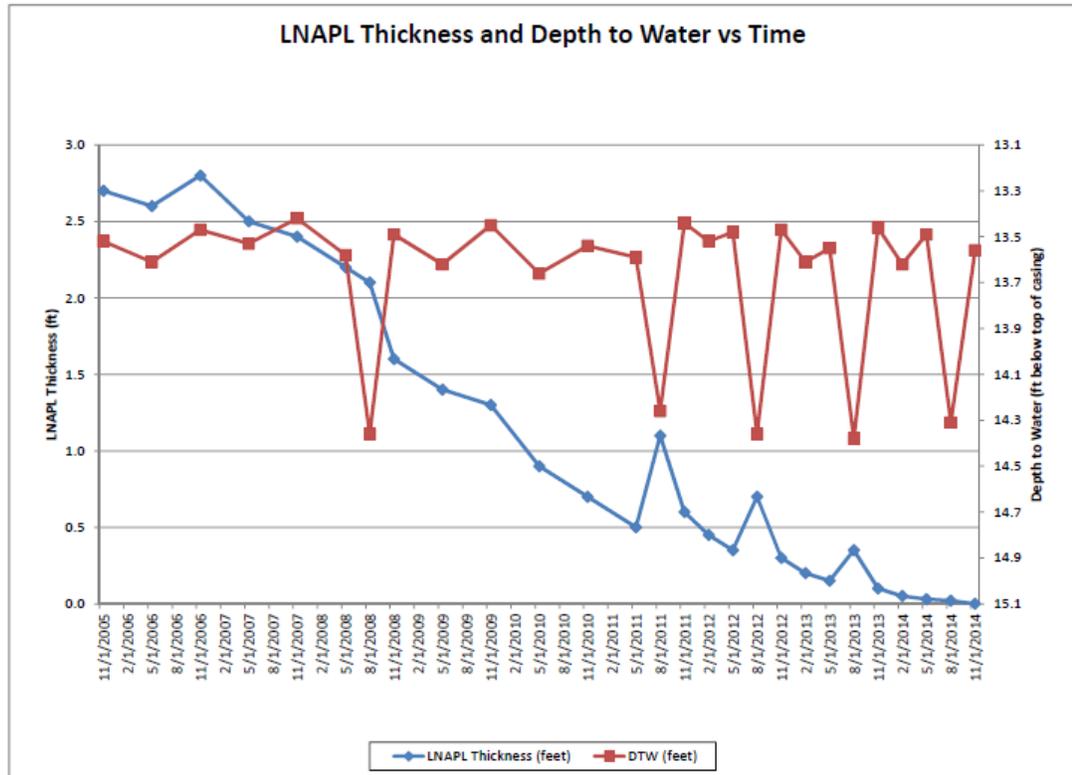


Figure 5. LNAPL thickness and depth to water vs. time

d) Measuring LNAPL Transmissivity

Since LNAPL transmissivity is related to all the key variables that can affect recoverability, it is often a better metric than the conventionally used metric of in-well thickness (ITRC 2009) for determining the progress / effectiveness of a soil flushing program. LNAPL transmissivity is a complex parameter that is not a constant of the formation but rather varies with test conditions, time and changing piezometric conditions (Beckett, G.D. and D Huntley 2015), therefore it is important to limit the variability in measurement techniques over time at a given subject site to ensure useful results are obtained. The basic premise is measurement of LNAPL transmissivity following soil flushing applications and considering cessation of active

remediation once transmissivity values become asymptotic or reach published values accepted to be indicative of LNAPL recoverability limits.

e) Soil flushing during in situ chemical oxidation

In situ chemical oxidation injection events often exhibit soil flushing effects similar to surfactant injections. These are typically a result of increased subsurface temperatures and pressures associated with the chemical oxidation reactions taking place in the subsurface. In this instance, additional injected chemicals react with the mobilized LNAPL causing it to break down. In some cases, depending on the volume of LNAPL mobilized, it may be prudent to perform a fluid recovery event a few days after the chemical injection event to target recovery of the mobilized LNAPL. It is important to minimize the volume of ground water recovered during such an event so as not to remove the injected chemicals so that they may remain in the subsurface as intended to react with the target contaminants.

As outlined above, there are complexities and uncertainties in each of the methods used to evaluate the progress and effectiveness of NAPL recovery. It is therefore recommended the investigator consider using a number of the aforementioned techniques to establish multiple lines of evidence to guide decision-making.

### **6.3.3. SOIL VAPOR EXTRACTION / AIR SPARGING**

Soil vapor extraction (SVE) is used to remove volatile organic compounds (VOCs) and to a lesser extent semi-volatile organic compounds (SVOCs) from unsaturated subsurface soils, which for this technical guidance is also meant to include fill material. Where VOC and SVOC impacts are present in the saturated zone, air sparging is commonly combined with SVE for the removal of VOCs and SVOCs from ground water and saturated subsurface soils. SVE may also be combined with a ground water recovery, where the SVE removes contaminants from soil which is normally saturated. Even when SVE is combined with ground water recovery, it is common for some condensate to accumulate in the SVE system piping and equipment. Accumulated condensate and/or ground water collected by a simultaneously-operating ground water recovery system shall be properly treated and/or disposed of. Condensate and/or ground water may be collected and containerized for offsite treatment / disposal or may be treated on site using various common ground water treatment unit processes (granular activated carbon adsorption, air stripping, etc.). Where on site treatment is the chosen means, the appropriate discharge permits outlined in Section 7 shall be obtained by the investigator.

#### **6.3.3.1. SVE / AIR SPARGING APPLICATION, NETWORK WELLS, AND SAMPLING**

SVE is accomplished by inducing a vacuum in unsaturated subsurface soils typically through a network of vertical and/or horizontal extraction wells connected to a central vacuum blower.

The induced vacuum generates a flow of soil vapors through the subsurface soils to the extraction wells thereby conveying recoverable contaminants to a treatment system. Various styles and sizes of vacuum blowers are available for use depending on the subsurface soil conditions. Coarse grained/high permeability subsurface soils require vacuum blowers capable of high flow rates at low to moderate vacuum pressure. Fine grained/low permeability soils require vacuum blowers capable of high vacuum pressure and typically lower vapor flow rates. The design of the SVE wells and equipment is typically based on the results of a pilot study conducted to determine the radius of influence (ROI) of a SVE well and the corresponding vacuum and vapor flow rates. Once the ROI is established, the number and placement of SVE wells required to encompass the target treatment area can be determined. The corresponding vacuum and vapor flow rate information is used for the engineering design of the SVE vacuum blower, piping network and other associated equipment. Extracted soil vapors are typically treated prior to discharge to the atmosphere and may require a Department-issued air pollution control permit.

Air sparging is accomplished by injecting atmospheric air into the saturated zone using a network of vertical and/or horizontal injection wells connected to a central air compressor. The injected air causes the volatilization of VOCs in saturated zone and their subsequent release into the unsaturated zone. For this reason, air sparging is typically conducted in conjunction with SVE such that the VOCs released from the saturated zone are removed from the subsurface by the SVE system. Air sparging also typically increases the dissolved oxygen levels in the saturated zone, which may stimulate biodegradation.

Similar to SVE vacuum blowers, various styles and sizes of air compressors are available for use depending on the subsurface soil conditions. Coarse grained subsurface soils require air compressors capable of high flow rates at low to moderate pressures. Fine grained subsurface soils require air compressors capable of higher pressure and typically lower air flow rates. Similar to SVE, the design of the air sparge system is typically based on the results of a pilot study conducted to determine the sparging radius of influence (ROI) and the corresponding injection pressure and air flow rates. Once the ROI is established, the number and placement of air sparge wells required to address the target treatment area can be determined. The corresponding pressure and air flow rate information is used for the engineering design of the air sparge compressor, piping network, and other associated equipment.

There are subsurface soil conditions that are not conducive for the use of SVE and/or air sparging. In certain low permeability subsurface soils, it may not be possible to generate sufficient soil vapor flow for efficient VOC recovery. In other cases, the vacuum levels required to generate sufficient air flow may result in significant upwelling (mounding) of the ground water table, which in turn may occlude the extraction well screen and/or the targeted soils. Similarly, the pressures required for the injection of sparge air may be so high that they cause fracturing in the soil matrix and the development of preferential flow paths, resulting in non-uniform distribution of air throughout the contaminated media.

The pressure at which fracturing in the soil matrix may begin to occur will vary greatly based on the soil type and moisture content at the time sparging is occurring. Monitoring of injection well and observation well pressures to determine if this condition is occurring is addressed in Section 6.3.3.2. It may, however, be desirable under certain circumstances to cause fracturing of the soil matrix in order to increase the total volume of sparge air delivered, thereby increasing the in-situ stripping rate (transfer of volatile contaminants from the dissolved phase to the vapor phase). Pulsed operation of the sparge system is typically employed in these situations in an effort to get more uniform distribution of sparge air through the subsurface. Pulsing durations per well can be on the order of minutes to days and will vary based on site-specific conditions, not only from site to site, but often at the same site as remediation progresses and subsurface contaminant distribution changes.

### **6.3.3.2. SVE/AIR SPARGE PERFORMANCE MONITORING**

Performance monitoring for SVE / Air Sparge systems can be characterized as process performance monitoring and remedial effectiveness performance monitoring. Process performance monitoring for SVE and air sparging systems is largely based on confirming the design SVE and air sparging ROI are being achieved while remedial effectiveness performance monitoring is based on confirming contaminant reduction is occurring. Additional details on both types of performance monitoring are presented below.

#### **6.3.3.2.1. PROCESS PERFORMANCE MONITORING**

Process performance monitoring for SVE and air sparging systems is largely based on confirming the design SVE and air sparging ROI are being achieved. As described in Section 4.2.2, the use of the term radius of influence is not meant to imply a circular pattern. As indicated in more detail below, measurements should be taken in multiple directions and varied depths from the extraction / injection wells in order to understand potential anisotropy of the subsurface. Subsurface heterogeneities, particularly in glacial deposits, should be accounted for in selecting performance monitoring locations.

SVE ROI is typically evidenced through the measurement of air flow and/or induced vacuum at observation wells located within the design ROI of several of the SVE wells. Because measurement of air flow in the subsurface is complex, measurement of induced vacuum as evidence of air flow is more commonly performed. Multiple methodologies are commonly employed to establish SVE ROI based on applied and induced vacuum measurements, these include:

1. the distance from the extraction well where the induced vacuum reaches a minimum of 0.1 inches of water column (in w.c.); and

2. the distance from the extraction well where the induced vacuum reaches 1% of the applied vacuum.

Direct measurement of induced vacuum at the distances where the conditions described above are achieved is not required. The distance where the indicated condition is reached can be calculated by plotting data points from numerous injection / observation well pairs and extrapolating the data to the indicated condition. Consider the data below (table 4).

*Table 4. SVE scenario*

| <b>SVE Scenario</b>                               |                          |                                   |                    |
|---|--------------------------|-----------------------------------|--------------------|
| Distance from Extraction Well to Observation Well | Applied Vacuum (in w.c.) | Observation Well Vacuum (in w.c.) | Induced Vacuum (%) |
| 0   | 60                       | 60                                | 100%               |
| 10  | 60                       | 5                                 | 8.3%               |
| 20  | 60                       | 2                                 | 3.3%               |
| 30  | 60                       | 0.9                               | 1.5%               |
| 40  | 60                       | 0.1                               | 0.2%               |

In the above SVE data scenario, the ROI at the 1% of applied vacuum condition can be inferred from the below graph as 33 feet (fig. 5). However, the ROI based on Johnson's studies can be direct measured as 40 feet.

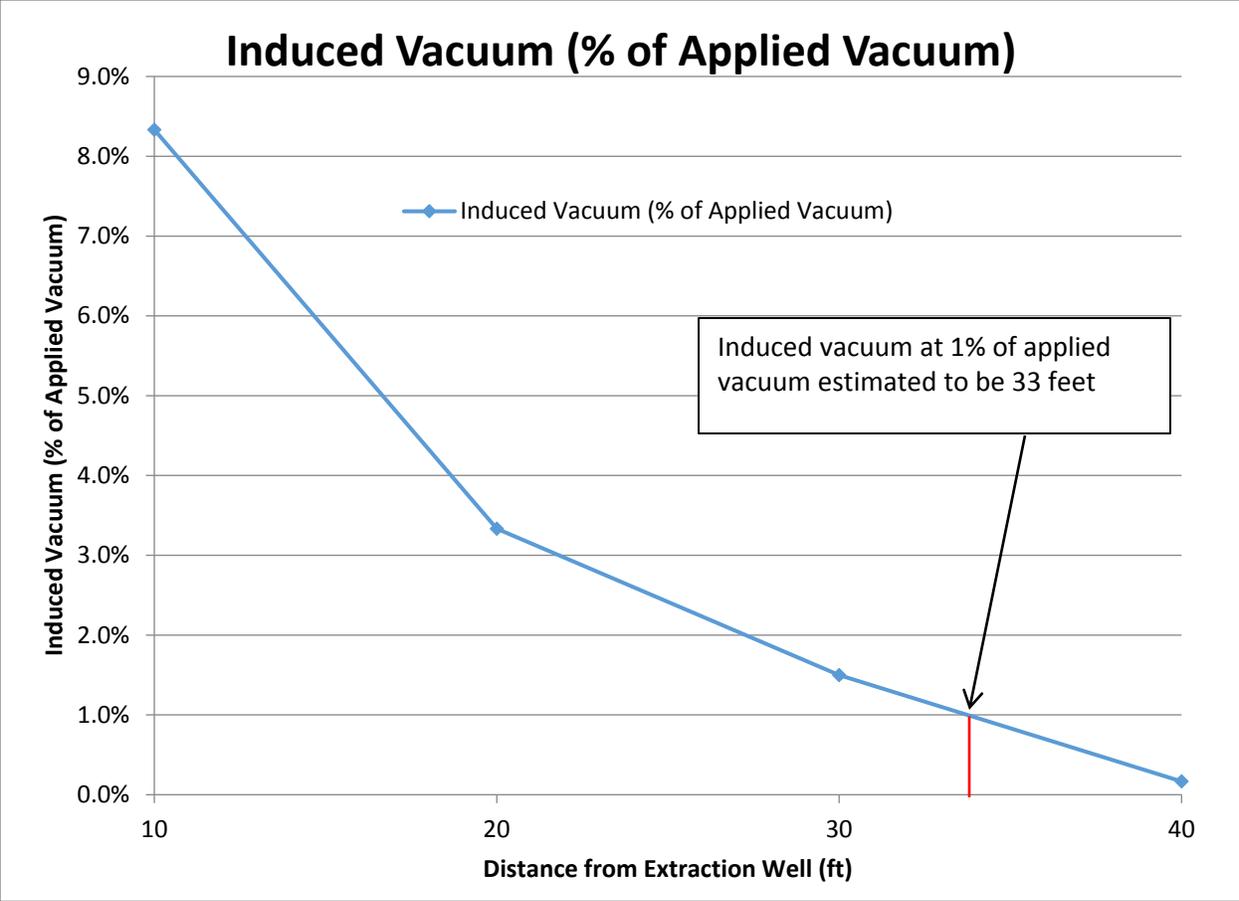


Figure 6. Induced vacuum (% of applied vacuum)

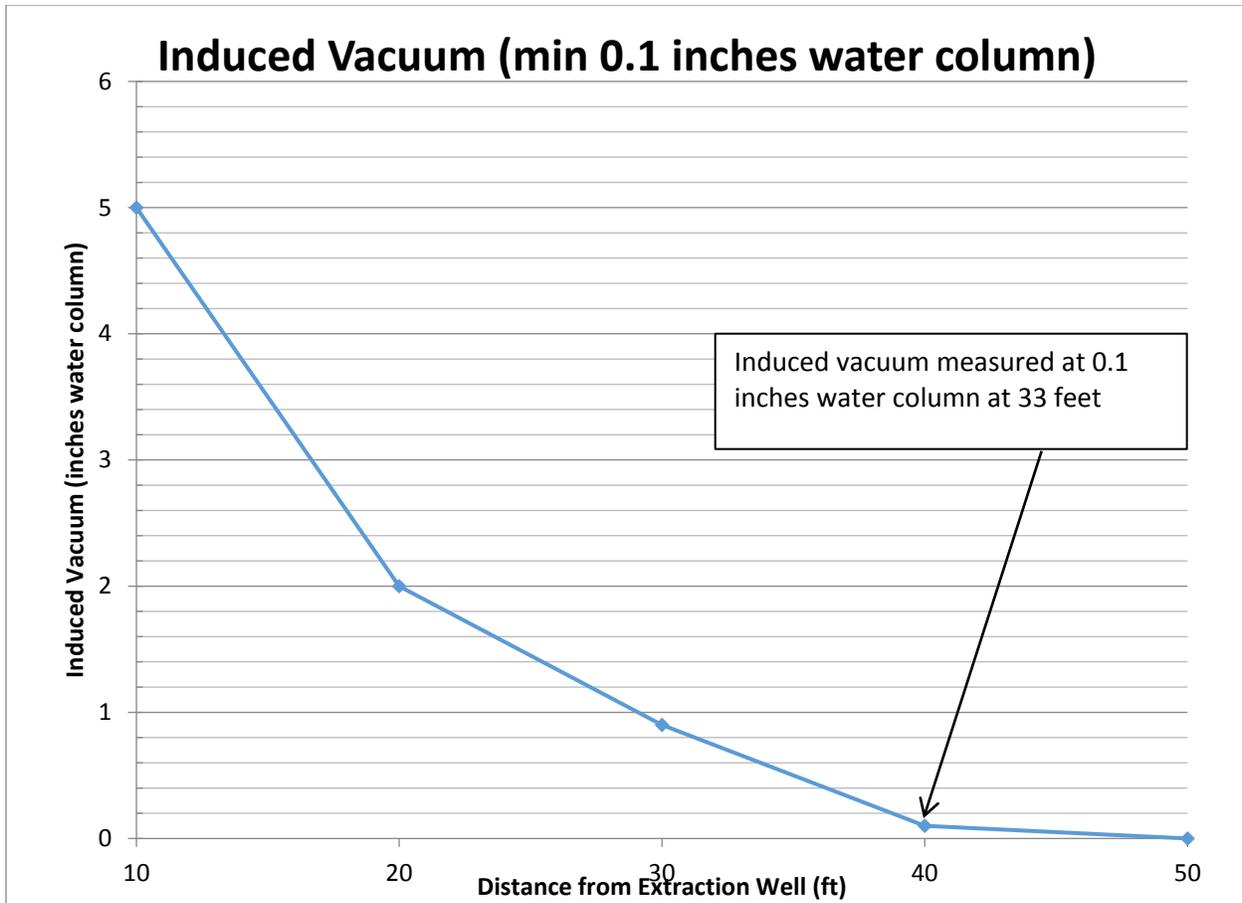


Figure 7. Induced vacuum

In the instance where an induced vacuum of 0.1 in w.c. is not directly measured, the distance can be determined by generating a similar plot (fig. 6).

Once an SVE system is installed and operating, the above analysis can be performed for each extraction well to confirm suitable overlap of extraction well radii of influence to ensure the entire target remediation area is being influenced by the system (i.e., verify there are no dead zones/gaps in coverage). If deficiencies are noted, adjustments to the vacuum blower operating parameters or various equipment maintenance tasks can be performed to ensure the design ROI is being maintained. It is recommended the ROI be evaluated in this manner monthly for the first 3 – 6 months of SVE system operation, after which time the future monitoring schedule can be determined, though no less than quarterly is recommended for the duration of the system operation.

Multiple methods of determining the air sparge ROI are utilized, these include:

1. the distance from the injection well where the induced pressure reaches a minimum sustained pressure of 0.5 inches w.c.;

2. the distance from the injection well where the induced pressure reaches a minimum of 1% of the applied pressure;
3. the distance from the injection well where sustained mounding of the ground water table is observed;
4. the distance from the injection well where the dissolved oxygen increases; and
5. the distance from the injection well where a tracer gas injected with the sparge air is detected.

Similar to the SVE ROI determination, regardless of which method(s) are used, monitoring the air sparge ROI monthly for the first 3 – 6 months of system operation is advisable so system operating parameters can be adjusted to ensure the design ROI is maintained. In certain instances, the additional monitoring data collected may be reason to reevaluate the CSM.

#### **6.3.3.2.2. REMEDIAL EFFECTIVENESS PERFORMANCE MONITORING**

Remedial effectiveness performance monitoring for SVE and air sparging systems is largely based on confirming contaminant reduction is occurring. SVE effectiveness performance monitoring is typically monitored by determining the target contaminant recovery rate; and air sparging system performance monitoring is typically monitored through sampling of groundwater monitoring wells.

The SVE system contaminant mass recovery rate is calculated using the measured contaminant concentration and vapor flow rate. Where vapor phase contaminant concentrations in the extracted soil vapor are reported in mg/m<sup>3</sup>, the following formula can be used:

$$\text{Conc (mg/m}^3\text{)} \times \text{Flow (m}^3\text{/min)} = \text{Mass recovery rate (mg/min)}$$

Any number of unit conversions can be applied to the desired units of measure (lbs./hr., g/min, etc.).

It is typical for the contaminant recovery rate to decrease exponentially during the first 6 – 12 months of SVE system operation. By routinely measuring the contaminant concentrations being recovered by each extraction well, the SVE system can be optimized by increasing flow from the wells with the highest concentrations and decreasing flow from the wells with the lowest concentration. The contaminant recovery rate can subsequently be used to calculate the total contaminant mass recovered by the system, which can be compared to the total subsurface contaminant mass estimated in the CSM.

Once an appreciable percentage of the estimated total contaminant mass is recovered and the mass recovery rates reach asymptotic trends, remedial progress soil borings may be considered.

The results of the remedial progress soil borings can be used to determine which extraction wells, if any, need to remain in operation, and whether or not other adjustments to the system operating parameters are needed to address soil sample locations that remain above regulatory standards. The remedial progress sampling may also serve to verify the attainment of remedial goals in the final remediation documents.

Since the focus of an air sparging system is to reduce target contaminant concentrations in the saturated zone, creating trend graphs of ground water monitoring well sampling results can be used to assess progress of subsurface contaminant mass reduction. Adjustments to the operating parameters for individual wells (sparge air flow rate and pressure) can be made to provide additional focus on wells where the highest contaminant levels persist. Similar to SVE system mass recovery monitoring, as target compound concentrations in ground water reach asymptotic levels, remedial progress soil borings may be warranted to determine which, if any, air sparge wells should remain in operation. As indicated the sampling results may also be utilized to verify the attainment of remedial goals in the final remediation documents.

#### **6.3.4. IN-WELL AIR STRIPPING/GROUND WATER CIRCULATION WELLS**

In-well air stripping (IWAS) technology creates a groundwater circulation cell around a well, flushing soil and moving contaminated water to the groundwater circulation well, where the VOCs are stripped with a counter-current air stream. An in-well groundwater pump moves water from the lower portion of the well to the upper portion of the well, where it is discharged through a spray nozzle or distribution fitting and contacts air that has been injected (sparged) at a fixed depth below the groundwater table in the screened interval. This pumping/air stripping causes a mounding effect that creates the circulation cell. The technology also incorporates vapor extraction at the wellhead to capture and treat emissions originating from the IWAS well. The partially treated groundwater is never brought to the surface; it is forced into the unsaturated zone, and the process is repeated as water follows a hydraulic circulation pattern or cell that allows continuous cycling of groundwater. As groundwater recirculates through the treatment zone in situ, volatile contaminant concentrations are gradually reduced due to the stripping from the injected air (FRTR, Remediation Technologies Screening Matrix and Reference Guide, Version 4.0).

The technology could be implemented as a stand-alone application, or as a companion technology to enhance the distribution of injected fluids (e.g., chemical oxidants, biological amendments) and is not anticipated to be used in areas with free phase or measurable LNAPL or DNAPL, due to the potential to spread the contamination.

##### **6.3.4.1. GROUND WATER CIRCULATION WELLS PERFORMANCE MONITORING**

Performance monitoring will allow the investigator to assess IWAS system performance, optimize the design parameters (generally adjusting the air flow rate and pressure), determine the

treatment duration, and evaluate final results. The monitoring should include appropriate sampling and analysis and evaluation that will measure the effect of the IWAS technology in terms of whether defined remedial objectives or operational end points have been achieved. Suggested performance monitoring analytical parameters and metrics that may be applicable are listed below. Based on site-specific conditions and remedial objectives, additional parameters and metrics may be warranted.

- Analyze and compare concentrations of contaminants of concern in groundwater monitoring wells at regular intervals to determine extent of decrease in groundwater concentrations over time. Please note, temporary increases in contaminant concentrations can indicate that trapped or residual NAPL is being mobilized, or that groundwater within the treatment zone is effectively being mixed.
- IWAS relies on pumping and air stripping to create a groundwater circulation cell. Therefore, water level measurements and geochemical parameters (e.g., DO, ORP, and pH) should be monitored prior to (i.e., baseline) and during system operation. The data provides information on the hydraulic effect of the recirculation, which can be used to demonstrate that dynamic groundwater mixing is occurring throughout the target treatment area (i.e., verification that the design ROI is being achieved).
- Collect air samples from each IWAS well and the effluent vapor port to establish the baseline readings, and regularly during system operation. Monitoring effluent air concentrations is particularly important to ensure concentrations are below any applicable air permit treatment requirements and limits.
- The following measurements should regularly be collected to evaluate IWAS system performance: flow rate, vacuum, sparge air pressure, dissolved oxygen, ORP, pH, and system VOC concentrations from the influent, mid-treatment (if applicable) and effluent sample ports. Depending on the target contaminants, headspace measurements at the monitoring wells may be warranted to evaluate whether the SVE component of the IWAS system is operating effectively and within air permit conditions if applicable.
- System influent air samples can be used to estimate mass removal rates and demonstrate reduction in contaminant mass, in addition groundwater monitoring during system operation can also help assess remedial performance.
- Identify the need for any system modifications by comparing the original design data with the performance monitoring data.

Table 5. Performance monitoring parameters for physical technologies

| Parameters                               | Solidification / Stabilization | Soil Flushing | Soil Vapor Extraction | Air Sparge | In Well Air Stripping |
|--|--------------------------------|---------------|-----------------------|------------|-----------------------|
| <b>Field Parameters<sup>+</sup></b>      |                                |               |                       |            |                       |
| Depth to water*                          | *                              | *             | *                     | *          | *                     |
| Depth of well*                           | *                              | *             | *                     | *          | *                     |
| NAPL Thickness                           | 2                              | 1             | 2                     | 2          | 3                     |
| Injectant Indicator / Tracer (a)         | 4                              | 1             | 4                     | 3          | 4                     |
| Injectant Flow Rate                      | 2                              | 1             | 4                     | 2          | 4                     |
| Injectant Total Volume                   | 2                              | 1             | 4                     | 2          | 4                     |
| Injectant Pressure                       | 2                              | 1             | 4                     | 2          | 4                     |
| Injectant Concentration (percentage)     | 4                              | 1             | 4                     | 4          | 4                     |
| Extraction Flow Rate                     | 4                              | 1             | 2                     | 2, 6       | 2                     |
| Extraction Total Volume                  | 4                              | 1             | 2                     | 2, 6       | 3                     |
| Extraction Pressure / Vacuum             | 4                              | 4             | 2                     | 2, 6       | 2                     |
| Vapor Extraction Concentration           | 4                              | 4             | 2                     | 2, 6       | 2                     |
| pH*                                      | *                              | *             | *                     | *          | *                     |
| Dissolved oxygen*                        | *                              | *             | *                     | *          | *                     |
| Oxidation-reduction potential*           | *                              | *             | *                     | *          | *                     |
| Temperature*                             | *                              | *             | *                     | *          | *                     |
| Conductivity*                            | *                              | *             | *                     | *          | *                     |
| Contaminants in Well Headspace*          | 4                              | 2             | 2                     | 2          | 4                     |
| <b>Lab Parameters - Ground Water</b>     |                                |               |                       |            |                       |
| Contaminants and breakdown products      | 2                              | 1             | 2                     | 2          | 2                     |
| Injectant Indicator / Tracer (a)         | 4                              | 1             | 4                     | 3          | 4                     |
| Foaming Agents (ABS/LAS)                 | 4                              | 1             | 4                     | 4          | 4                     |
| Extraction Concentration                 | 4                              | 3             | 4                     | 4          | 4                     |
| Nitrate-nitrite nitrogen                 | 4                              | 4             | 4                     | 4          | 3                     |
| Ammonia nitrogen                         | 4                              | 4             | 4                     | 4          | 3                     |
| Sulfate                                  | 4                              | 4             | 4                     | 4          | 3                     |
| Total iron                               | 4                              | 4             | 4                     | 4          | 3                     |
| Ferrous iron                             | 4                              | 4             | 4                     | 4          | 3                     |
| Arsenic                                  | 2                              | 2             | 2                     | 2          | 2                     |
| Sulfide                                  | 4                              | 4             | 4                     | 4          | 3                     |
| Chloride                                 | 4                              | 4             | 4                     | 4          | 3                     |
| Bromide                                  | 4                              | 4             | 4                     | 4          | 3                     |
| Dissolved carbon dioxide                 | 4                              | 4             | 4                     | 4          | 3                     |
| Dissolved ethene, ethane, and methane    | 4                              | 4             | 4                     | 4          | 3                     |
| Alkalinity                               | 4                              | 4             | 4                     | 4          | 3                     |
| <b>Lab Parameters - Other</b>            |                                |               |                       |            |                       |
| Soil Contaminants and breakdown products | 2                              | 3             | 2                     | 2          | 4                     |
| SPLP on Core Samples                     | 2                              | 4             | 4                     | 4          | 4                     |
| Soil Vapor Contaminants / Headspace      | 4                              | 3             | 3                     | 3          | 4                     |
| Soil Vapor Contaminants / Extracted      | 4                              | 4             | 2                     | 2, 6       | 4                     |

Notes: See Section 5.4 for a detailed discussion of notes 1, 2, and 3 below.

+ - For Field Parameters see Appendix B

\* - Standard field parameters required for all ground water sampling events

1 - DGW Required Analysis if a COC or related to a direct or indirect impact of DGW.

2.- Recommended analysis

3 - Conditional analysis

4 - Analysis not applicable

5 - Soil vapor extraction should be conducted during most air sparge applications

(a) Injectant indicators and tracers vary by technology. These may include field colorimetric indicators and or shake testing (see Appendix B) for soil flushing agents, field and/or laboratory analysis of helium for air sparge helium tracers, laboratory analysis of indicators for soil flushing agents, etc.

### 6.3.5. CHEMICAL OXIDATION

The in-situ chemical oxidation (ISCO) remedial technology consists of injection of oxidants to the subsurface to oxidize contaminants into innocuous end-products such as chloride, carbon dioxide, and water. Oxidant delivery is commonly achieved by temporary or permanent injection wells, direct push borings, infiltration galleries, passive techniques (e.g., oxygen socks; permanganate candles) and spreading and/or mixing in open excavations. The contaminants amenable to chemical oxidation include chlorinated solvents, total petroleum hydrocarbons (TPH), polycyclic aromatic hydrocarbons (PAHs), oxygenates (e.g., methyl tertiary butyl ether (MTBE)), phenols, 1,4-dioxane, nitroaromatics (explosives), and pesticides. Recently groundwater contamination by perfluorinated compounds (PFCs) is gaining attention; ISCO is considered one of the effective remedies (SERDP, ER-2423. In Situ Treatment Train for Remediation of Perfluoroalkyl Contaminated Groundwater: In Situ Chemical Oxidation of Sorbed Contaminants (ISCO-SC), April 2016).

The major chemical oxidants used for soil and groundwater remediation are permanganate (sodium or potassium), sodium persulfate, hydrogen peroxide (Fenton's Reagent), ozone, perozone, and percarbonate and/or combinations thereof. Each individual oxidant has its own defined oxidative strength – the stronger the oxidative strength, the more recalcitrant contaminants it can oxidize and the faster the reaction kinetics. Note that there are “mild” oxidants which are used as a source of oxygen for biological oxidation of contaminants rather than as chemical oxidants. These “mild” oxidants are combinations of calcium oxyhydroxide and calcium hydroxide; magnesium peroxide and magnesium hydroxide; and calcium peroxide and calcium hydroxide.

Key factors for successful ISCO remediation are the effective distribution of the oxidants in the treatment zone (i.e., ensuring the oxidants contact the contaminants) and the reactivity of an oxidant with the contaminants. This in turn depends on the persistence of the oxidant in the subsurface. For example, permanganate is known to persist for long periods of time, and therefore, it is possible to transport to a greater distance from the injection location. In contrast, hydrogen peroxide has been reported to persist in soils for only minutes to hours, limiting its potential travel distance. Note, however, that peroxide oxidizes a wider range of contaminants compared to permanganate. To overcome the relatively shorter travel distance of peroxide, closer injection spacing may be considered. This example underscores the importance that the ISCO design and oxidant selection be based on the nature of the contaminants and project objectives. Practitioners are encouraged to refer to ITRC in-situ chemical oxidation guidance documents that provide greater detail on the oxidant application design at <http://www.itrcweb.org/Guidance/ListDocuments?TopicID=10&SubTopicID=17>, as well as at EPA's Clean-Up Information website at [https://clu-in.org/techfocus/default.focus/sec/In\\_Situ\\_Oxidation/cat/Guidance/](https://clu-in.org/techfocus/default.focus/sec/In_Situ_Oxidation/cat/Guidance/).

Oxidant dosing should meet the demand exerted by target compounds (contaminants) as well as non-target compounds; oxidant demand exerted by the latter is commonly referred to as native oxidant demand (NOD). Soil native organic carbon, carbonates, and certain reduced metals or minerals are the primary contributors to NOD. NOD is typically analyzed where persulfate or permanganate are the chosen oxidants. On the other hand, for hydrogen peroxide and ozone, since oxidant demand is effectively infinite, persistence or stability of the oxidant is measured instead of NOD.

Site-specific conditions and parameters, in conjunction with oxidant-specific characteristics, should be carefully considered to determine whether ISCO is a viable technology for deployment relative to other remedial technologies. Some of the advantages and disadvantages of the ISCO technology are listed in a USEPA published document (ISCO Engineering Issue, USEPA 2006). Additional information on ISCO causing metals mobilization is a ‘contact sport’ and oxidant delivery and distribution available in the subsurface could be challenging due to reactive transport and aquifer heterogeneities. The NOD may be high in some soils/aquifers requiring high oxidant dosage to meet the demand for the non-target compounds. Short persistence of some oxidants (particularly peroxide) could result in multiple injections. A more recent 2015 report (Gardner et al., 2015) is available at <https://www.estcp.com/content/download/38033/361074/file/ER-2132%20Final%20Report.pdf>.

Site-specific conditions and contaminant type determine the type of oxidant required to address the contaminants of concern. A brief description of commonly used oxidants is provided below.

#### **6.3.5.1. PERMANGANATE**

Permanganate-based ISCO is more fully developed than other oxidants and applicable under a wide range of environmental conditions (e.g., pH 3.5 to 12). There are two forms of permanganate: i) potassium permanganate, available as a solid with a solubility of approximately 6 percent; and ii) sodium permanganate, available as an aqueous solution that is relatively more soluble (40 percent). For a design that requires high oxidant mass over a limited pore volume, sodium permanganate use may be appropriate based on its solubility. Caution should be exercised when procuring permanganate as there are varying grades available, which may contain a variety of impurities (see metals listed in Table 4.2.1 in Gardner et al., 2015).

#### **6.3.5.2. HYDROGEN PEROXIDE/FENTON’S REAGENT**

Oxidation via hydrogen peroxide-based Fenton’s reagent is chemically complex compared to most other reactions and is capable of degrading a wide range of contaminants. Since peroxide is reacted upon by iron or other chemical strains, this technology is often referred to as catalyzed hydrogen peroxide (CHP). As the CHP reaction kinetics are generally faster at a lower pH (e.g.,

3 to 4), it is common to inject an acid along with peroxide. In most ISCO projects, it is common to see practitioners use lower strength peroxide (1 to 10 percent) for the following reasons: i) reduce peroxide scavenging (i.e., reaction with non-target constituents); ii) increase injection volumes to facilitate greater travel distances (i.e., cover a larger area); and iii) reduce side-effects such as high temperatures and pressures.

Recently, a few reagents have been included as part of peroxide solution to enhance the oxidant performance through increased persistence. These reagents are primarily intended to improve the stability (longevity) and enhance the transport distance of peroxide in the aquifer. The most commonly used peroxide stabilizers are phosphates, chelated iron catalysts, and citrate which are effectively distributed in the aquifer along with peroxide, minimizing the generation of organic vapors or high temperatures. This process where Fenton's oxidation is modified to occur at or near neutral pH, with improved longevity, is commonly termed as Modified Fenton's Reagent (MFR) or Stabilized Hydrogen Peroxide (SHP).

#### **6.3.5.3. PERSULFATE**

Sodium persulfate is the newest form of oxidant currently being used for ISCO. Unlike permanganate but similar to peroxide, a catalyst is required to activate persulfate to produce the powerful persulfate and sulfate radicals that participates in contaminant oxidation. The activators include chelated iron, high pH (base addition), silicate based, and hydrogen peroxide (heat) which allow persulfate to be effective over a wide range of subsurface conditions. Recent reports, which require further confirmatory studies, identified new products for persulfate activation. These include a food grade carbohydrate (ISOTEC, 2016) and manganese dioxide, a by-product of permanganate oxidant (Geosyntec Consultants, 2016) Persulfate is more stable in the subsurface (weeks to months) when compared to peroxide and ozone (hours to days) but less stable compared to permanganate (several months).

#### **6.3.5.4. OZONE**

Ozone is a strong oxidant that has been used in the subsurface remediation targeting both unsaturated and saturated zones. Ozone is a gas with limited water solubility. Similar to hydrogen peroxide, ozone oxidation does not leave a residue (such as sulfate from persulfate or manganese dioxide from permanganate). Ozone is unstable (half-life of minutes to hours) and requires generation on site. In addition, low water solubility may require long-term delivery of ozone into the groundwater during the remediation. As indicated by ITRC, use of ozone may be beneficial in low-permeability environments where gas phase permeability is typically greater than liquid phase permeability.

#### **6.3.5.5. PEROZONE**

Perozone is an oxidative technology where both ozone and hydrogen peroxide are used together in combination to address both unsaturated and saturated portions of the contaminated sites. Ozone and hydrogen peroxide injection is considered to be one of the most aggressive forms of ISCO as a larger amount of oxidant is introduced into the subsurface capable of producing substantially more hydroxyl radicals compared to hydrogen peroxide alone. The characteristics of perozone use are similar to those observed with hydrogen peroxide and ozone.

#### **6.3.5.6. PERCARBONATE**

Sodium percarbonate is commonly referred to as solid hydrogen peroxide as it is a stabilized form of hydrogen peroxide whereby three molecules of hydrogen peroxide are bound to two carbonate molecules of sodium salt with a chemical composition of  $((\text{Na}_2\text{CO}_3)_2(\text{H}_2\text{O}_2)_3)$ . Percarbonate can be used directly without activation or used in combination with a silicate-based activation technology. When percarbonate is injected into the contaminated groundwater, it reacts slower than hydrogen peroxide, but offers rapid contaminant degradation. Percarbonate generates comparatively less heat and pressure compared to hydrogen peroxide and persists for up to 4 weeks. Percarbonate is non-corrosive to concrete and most metals therefore it is often considered when injecting near underground utilities.

#### **6.3.5.7. 'MILD' OXIDANTS**

The 'mild' oxidants consist of magnesium peroxide, calcium oxyhydroxide, calcium peroxide, and calcium hydroxide that primarily decompose over an extended period (9 to 12 months) in contact with water to provide molecular oxygen. The slowly released molecular oxygen will be used by microorganisms as an electron acceptor (for respiration) and facilitate aerobic biodegradation. Although this is included within the oxidants group, typically these reagents are used for stimulating biodegradation of low concentration plumes as discussed in Section 6.2.2.3.

#### **6.3.5.8. MONITORING THE ISCO PERFORMANCE**

The ISCO performance monitoring consists of process performance monitoring and remedial effectiveness performance monitoring as discussed below. When conducting ground water sampling, care must be exercised when sampling after an ISCO treatment, as any oxidant still present in the ground water may bias the sample low. When oxidant is present, EPA guidelines on sample preservation should be followed, as presented in EPA's 2012 Ground Water Issue, "Ground Water Sample Preservation at In-Situ Chemical Oxidation Sites – Recommended Guidelines" (<https://clu-in.org/download/techfocus/chemox/ISCO-sample-preservation.pdf>).

### 6.3.5.8.1. BASELINE AND PROCESS PERFORMANCE MONITORING

The key objective of process performance monitoring is to ensure that treatment of contaminants is proceeding as per the design, and fine-tune the field process when treatment is falling short of design. Frequent (typically daily) monitoring of the process parameters will allow the implementation of field adjustments to meet remedial goals. Process monitoring is done as a quality control measure before, during, and immediately after the injection by sampling the groundwater from monitoring wells, injection wells, and vent wells (if any). The oxidant-specific process and performance parameters recommended for monitoring are provided in Table 6, while parameters common to most oxidants are outlined below.

- **Field Parameter Measurement** - Common field parameters include pH, DO, ORP, temperature, and conductivity. pH is measured to determine if it is in the desired range and to determine the impact of any acid or base injections (e.g., Fenton's reaction at a low pH or persulfate activation at a higher pH). DO is measured in order to monitor oxygen as a breakdown product, such as oxygen from peroxide or ozone reactions. Temperature is an indicator of exothermic reactions (e.g., peroxide decomposition). Conductivity is a general indicator of oxidant distribution. Field measurement of ferrous iron can also be considered to measure oxidant performance as its concentration is expected to decrease during oxidation.
- **PID Headspace Measurement** - PID headspace measurements from monitoring, injection, or SVE wells can be used as semi-quantitative data on VOC concentration trends.
- **Off-Gas Sample Measurement** - Off-gas sample measurements of carbon dioxide and oxygen from the monitoring, injection and SVE wells within and adjacent to treatment area can be used to assess real time ISCO performance.
- **Potential Vapor Intrusion Concerns** - Evaluate whether vapor intrusion risk would be increased by the ISCO technology and monitor potential receptors.
- **Contaminants of Concern Analysis** - Contaminants of concern should be analyzed to determine the degree and extent of oxidation at the target area, determine the effectiveness of the oxidant, and to optimize the delivery and dosage for future injections.
- **Oxidant Measurements** - Actual injection dosages and volumes should be recorded, and residual oxidant concentrations in groundwater should be monitored to determine the actual radius of influence and oxidant distribution.
- **Metals Concentrations** – Total metals concentrations (e.g., lead, chromium, arsenic, cadmium, zinc) in groundwater should be monitored (and dissolved metals if appropriate) as ISCO may promote temporary mobilization of metals within the treatment zone due to the change in oxidation status of the metals and/or pH changes. ITRC (2005)

recommends that at a minimum the initial investigation of soil and ground water include analysis for arsenic, barium, cadmium, chromium (including hexavalent chromium), copper, iron, lead, and selenium. Recently, it was reported that beryllium and antimony could also be mobilized if present (Gardner et al., 2015). Performance monitoring shall include only those determined to exist onsite or that could be present in the oxidant as an impurity.

- General Geochemistry – This is recommended for baseline sampling, not for process monitoring. Parameters may include nitrate nitrogen, ammonia, total and dissolved iron, manganese, sulfate, chloride, sodium, potassium, and alkalinity. ITRC (2005) specifically suggests total dissolved solids, chloride, sulfate, nitrate, fluoride, calcium, sodium, magnesium, potassium, and manganese.
- Ground water Level Elevations and NAPL Observations – Ground water elevations should be monitored to determine the hydraulic connection between the injection wells and monitoring wells. Observations for the presence of NAPL should also be made and the potential for NAPL mobilization assessed. Oxidants transform the aqueous, sorbed, and non-aqueous phases of the contaminants; in cases of NAPL, oxidants caused enhanced mass transfer, desorption, and dissolution.
- Systems Monitoring - Systems monitoring of injection temperature and pressures should be conducted to confirm if a controlled oxidation reaction is occurring. Regular inspections of hoses, fittings, valves, and pumps should be made to ensure proper operation and to identify potential leaks.

#### **6.3.5.8.2. REMEDIAL EFFECTIVENESS POST-TREATMENT PERFORMANCE MONITORING**

Post-treatment monitoring is needed to determine if the ISCO treatment has met the designed remedial goal. Post-treatment performance monitoring includes measurement of contaminant reduction in soil and groundwater after ISCO treatment and comparing contaminant concentrations to established pre-treatment (baseline) conditions to determine ISCO effectiveness. Establishing baseline conditions includes the analysis of soil and groundwater samples from the site for target contaminant(s) and reagent constituents.

To measure the effectiveness of ISCO remedy, soil and groundwater monitoring should continue quarterly for at least one year following the completion of ISCO treatment to validate the success of the remedy. This will also address possible concerns with back diffusion and whether the concentration decreases represent actual mass reductions and are not the result of the displacement of contaminated water. The post-treatment monitoring phase should provide adequate time for the treatment zone to achieve equilibrium. During this time, the monitoring data should be evaluated to assess progress towards achieving the remediation goals.

The oxidant-specific post-treatment parameters recommended for monitoring are provided in Table 6 and the sampling media and the associated parameters are summarized below.

- Soil Sampling - Soil boring samples should be collected from the ISCO targeted area after the completion of the oxidant injection program. The soil locations and depths will be similar to those of the remedial investigation phase and baseline sampling event. The post treatment soil samples should be analyzed for site contaminants of concern. Refer to Section 6.3.2 of the Department's Technical Guidance for Site Investigation of Soil, Remedial Investigation of Soil, and Remedial Action Verification Sampling for Soil ([http://www.nj.gov/dep/srp/guidance/srra/soil\\_inv\\_si\\_ri\\_ra.pdf](http://www.nj.gov/dep/srp/guidance/srra/soil_inv_si_ri_ra.pdf))
- Groundwater Sampling – At a minimum, it is recommended that groundwater samples be collected quarterly for up to one year after injection from the designated monitoring wells and analyzed for the following parameters.
  - Contaminants of Concern - Contaminant of concern concentration data are used to compare the post-treatment concentrations with baseline data to determine the degree of success of ISCO remedy.
  - Field Parameter Measurement - As indicated above common field parameters include pH, DO, ORP, temperature, and conductivity. Field measurement of ferrous iron can also be considered.
  - Metals Concentrations - Post-injection metals concentration data are used to determine if the ISCO remedy caused any metals dissolution or mobilization, and if so, whether the dissolution or mobilization was temporary and has attenuated to baseline levels with time and distance. For the appropriate list of metals and analytes, which would depend on site conditions and reagent used, see Table 6. An extensive review on the metals mobilization due to ISCO was performed by Gardner et al., 2015. The highlights of the review are described below and it is recommended that the site managers consider these highlights during the ISCO design.
    - CHP caused mobilization of most metals followed by persulfate; least metals mobilization was observed due to permanganate and many of those mobilized were part of the product present as impurities. With respect to persulfate, activation by iron caused more metals mobilization compared to caustic activation.
    - Select ISCO chemistry-specific metals mobilization was identified. These include arsenic mobilization due to base activated persulfate and chelated CHP; chromium and barium mobilization due to permanganate; chromium mobilization by almost all oxidants.
    - Citrate, acetate, and lactate reagents were reported to mitigate the metals mobilization. Although this organic carbon reagents presence can affect the

performance of ISCO, there might be cases where such a trend is acceptable so long, it leads to metals immobilization.

- Leaching of metals due to ISCO depends on soil type and native mineralogy and nature of historic fill (if present).
  
- General Geochemistry - General geochemistry parameters include nitrate nitrogen, ammonia, total and dissolved iron, manganese, sulfate, chloride, and alkalinity. These data can serve as indicators of secondary water quality, such as whether the oxidants left behind any residues (such as manganese and sulfate) or whether the oxidants completely mineralized the contaminants (such as chloride release from chlorinated solvents). In addition, oxidants such as peroxide, persulfate, and ozone may enhance post-oxidation microbial activity and natural attenuation by supplying electron acceptors such as dissolved oxygen and sulfate.
  
- Cation Concentrations - Cations such as calcium, magnesium, sodium, and potassium should be monitored in order to provide insight on the changes in total dissolved solids (TDS) due to the ISCO remedy. The analysis will help determine if this is a concern with respect to the formation porosity and permeability and whether TDS attenuates to baseline conditions or applicable ground water standards with time and distance.
  
- Undesirable Side-Effect: Oxidants use could potentially result in undesirable side-effects such as: i) formation of manganese dioxide (solid) during permanganate oxidation which could reduce porosity of the formation leading to short-circuiting; and ii) persulfate oxidation with iron activation or caustic could lead to a low or high pH aquifer which could be determined by field pH measurement. In case of permanganate, monitoring the injection rates and pressures during repeated applications may provide information if permeability is affected by manganese dioxide formation as its measurement is not common.

In case the monitoring reveals concentrations increase over two consecutive quarters, it is likely that the contaminants are still adsorbed to the soil and contributing mass to groundwater. Such plume behavior will require additional oxidant injections, additional post-treatment monitoring, or an alternate remedy.

Table 6. Performance monitoring parameters for chemical oxidation technologies

| Sampling Media / Parameters  | In-Situ Chemical Oxidation   |             |               |       |                             |               |                              |
|--|------------------------------|-------------|---------------|-------|-----------------------------|---------------|------------------------------|
|  | Fenton's / Hydrogen Peroxide | Per-sulfate | Per-manganate | Ozone | Perozone (Ozone / Peroxide) | Per-carbonate | Calcium / Magnesium Peroxide |
| <b>Field Parameters<sup>+</sup></b>  |                              |             |               |       |                             |               |                              |
| pH*  | *                            | *           | *             | *     | *                           | *             | *                            |
| Dissolved oxygen*  | *                            | *           | *             | *     | *                           | *             | *                            |
| Oxidation-reduction potential*   | *                            | *           | *             | *     | *                           | *             | *                            |
| Temperature*   | *                            | *           | *             | *     | *                           | *             | *                            |
| Conductivity*  | *                            | *           | *             | *     | *                           | *             | *                            |
| Ferrous iron   | 3                            | 3           | 3             | 3     | 3                           | 3             | 3                            |
| Oxidant (a)  | 1, 2                         | 1, 2        | 1, 2          | 1, 2  | 1, 2                        | 3             | 3                            |
| Non-Aqueous Phase Liquid (NAPL) monitoring   | 1, 2                         | 1, 2        | 1, 2          | 1, 2  | 1, 2                        | 3             | 3                            |
| Depth to water*  | *                            | *           | *             | *     | *                           | *             | *                            |
| Depth of well*   | *                            | *           | *             | *     | *                           | *             | *                            |
| <b>Lab Parameters - Ground Water</b>   |                              |             |               |       |                             |               |                              |
| Volatile organic compounds (VOCs)  | 2                            | 2           | 2             | 2     | 2                           | 2             | 2                            |
| Alkalinity   | 2                            | 2           | 2             | 2     | 2                           | 2             | 2                            |
| Nitrate-nitrite nitrogen   | 3                            | 3           | 3             | 3     | 3                           | 3             | 3                            |
| Fluoride   | 3                            | 3           | 3             | 3     | 3                           | 3             | 3                            |
| Total iron   | 1, 2                         | 2           | 2             | 2     | 2                           | 2             | 2                            |
| Dissolved iron   | 2                            | 2           | 2             | 2     | 2                           | 2             | 2                            |
| Total metals (b)   | 2                            | 2           | 2             | 2     | 2                           | 2             | 2                            |
| Dissolved metals   | 3                            | 3           | 3             | 3     | 3                           | 3             | 3                            |
| Sulfate  | 2                            | 1, 2        | 2             | 2     | 2                           | 2             | 2                            |
| Total organic carbon (TOC)   | 2                            | 2           | 2             | 2     | 2                           | 2             | 2                            |
| Total Dissolved Solids (TDS)   | 2                            | 2           | 2             | 2     | 2                           | 2             | 2                            |
| Chloride   | 3                            | 3           | 3             | 3     | 3                           | 3             | 3                            |
| Bromide (or other tracer) (a)  | 3                            | 3           | 3             | 3     | 3                           | 3             | 3                            |
| Major cations (c)  | 3                            | 3           | 3             | 3     | 3                           | 3             | 3                            |
| Compound specific isotopic analysis  | 3                            | 3           | 3             | 3     | 3                           | 3             | 3                            |
| <b>Lab Parameters - Soil</b>   |                              |             |               |       |                             |               |                              |
| Contaminants and breakdown products  | 3                            | 3           | 3             | 3     | 3                           | 3             | 3                            |
| Fraction organic carbon  | 3                            | 3           | 3             | 3     | 3                           | 3             | 3                            |
| Total metals (c)   | 3                            | 3           | 3             | 3     | 3                           | 3             | 3                            |
| Total iron   | 3                            | 3           | 3             | 3     | 3                           | 3             | 3                            |
| Total carbonate  | 3                            | 3           | 3             | 3     | 3                           | 4             | 4                            |
| Native Oxidant Demand (NOD)  | 2                            | 2           | 2             | 2     | 2                           | 3             | 4                            |
| Chemical oxygen demand   | 4                            | 4           | 4             | 4     | 4                           | 3             | 3                            |
| <b>Field Parameters (Others)<sup>+</sup></b>   |                              |             |               |       |                             |               |                              |
| Measurement for hydrocarbons, oxygen, carbon dioxide, and lower explosion levels (LEL) | 3                            | 3           | 3             | 3     | 3                           | 4             | 4                            |
| Pressure   | 3                            | 3           | 3             | 3     | 3                           | 4             | 4                            |
| <b>Other Media</b>   |                              |             |               |       |                             |               |                              |

|  |   |   |   |   |   |   |   |
|--|---|---|---|---|---|---|---|
| Vapor intrusion sampling for site or technology specific contaminants  | 2 | 3 | 3 | 2 | 2 | 3 | 3 |
| Surface water, sediment, pore water sampling for site or technology specific contaminants or secondary impacts | 3 | 3 | 3 | 3 | 3 | 3 | 3 |

Notes: See Section 5.4 for a detailed discussion of notes 1, 2, and 3 below.

+ - For Field Parameters see Appendix B

\* - Standard field parameters for all ground water sampling events

1 – DGW Required analysis

2 – Recommended analysis

3 –Conditional analysis

4 – Analysis not applicable

- (a) Injectant indicators and tracers vary by technology. These may include field colorimetric indicators and/or shake testing (see Appendix B) for soil flushing agents, field and/or laboratory analysis of helium for air sparge helium tracers, laboratory analysis of indicators for soil flushing agents, etc.
- (b) Total Metals – based on results of initial investigation (see Section 6.3.5.8.1)
- (c) Includes calcium, manganese, magnesium, sodium, and potassium

### 6.3.6. REDUCTION

Reduction processes are those processes that alter the chemistry of the groundwater to create reducing conditions within a given volume of groundwater or soil. A variety of compounds are susceptible to either chemical or biological degradation under reducing conditions. Examples of three of the more commonly used in-situ chemical reduction technologies (injection of calcium polysulfide (CaS<sub>x</sub>), zero-valent iron (ZVI), and emulsified vegetable oil (EVO)) are discussed below.

A number of proprietary remediation products are available that include both ZVI and various types of carbon sources and/or other constituents. These products were designed to treat recalcitrant organic compounds (e.g., chlorinated VOCs) in ground water and soils by creating conditions that accelerate chemical reduction (e.g., reductive dechlorination) and enhance anaerobic biodegradation of persistent organic contaminants. Monitoring requirements for the technologies are discussed in detail below and listed on Table 5. Monitoring requirements for other proprietary products are usually very similar though slight differences may be appropriate.

Several of these technologies may pose potential risks from secondary impacts such as creating highly corrosive conditions, temporary or localized increase in mobility of background metals. There is also the potential generation of Methyl Ethyl Ketone (MEK; i.e., 2-butanone) and Acetone (Fowler et. al., 2011). These potential risks are discussed below and can usually be addressed through appropriate design considerations and/or monitoring.

### **6.3.6.1. CALCIUM POLYSULFIDE INJECTION FOR THE TREATMENT OF HEXAVALENT CHROMIUM**

There are many reagents that can be used for in-situ treatment of hexavalent chromium ( $\text{Cr}^{\text{VI}}$ ), such as ascorbic acid, dithioate, ferro-black, and Metals Remediation Compound™. These technologies can be also be applied to other multivalent metals, such as uranium, selenium, vanadium, etc. Custom remediation and performance monitoring programs should be developed for each of these technologies. Calcium polysulfide (CaSx) injection is discussed below as an illustration of the primary issues that should be considered for the in-situ remediation of  $\text{Cr}^{\text{VI}}$ .

The objective of CaSx injection is to reduce the overall toxicity and mobility of total chromium via the conversion of highly toxic and mobile hexavalent chromium ( $\text{Cr}^{\text{VI}}$ ) to less toxic and less mobile trivalent chromium ( $\text{Cr}^{\text{III}}$ ). This process involves the reduction of  $\text{Cr}^{\text{VI}}$  to  $\text{Cr}^{\text{III}}$  via reaction with the CaSx.  $\text{Cr}^{\text{VI}}$  exists in aerobic environments primarily as the chromate anion ( $\text{CrO}_4^{2-}$ ). Chemical reduction of  $\text{Cr}^{\text{VI}}$  involves the use of a chemical electron donor such as CaSx. The reduction reaction generally occurs under slightly basic conditions, with pH's ranging from 8 to 10. Once the reduction takes place,  $\text{Cr}^{\text{III}}$  precipitates from solution as a hydroxide ( $\text{Cr}(\text{OH})_3$ ) or a mixed iron-chromium hydroxide ( $\text{Fe}_{0.25}\text{Cr}_{0.75}(\text{OH})_3$ ) under more neutral conditions (i.e., pH's of 7 to 8), thereby reducing the overall mass of the total dissolved Cr. Potential secondary impacts that should be considered are increased hardness and sulfate concentrations in nearby ground water and potable wells and increased sulfate and corrosively in soils in the immediate vicinity of the treatment zone. In addition, if naturally occurring or background levels of arsenic, manganese or iron are present, their mobility may be increased within the treatment zone.

#### **6.3.6.1.1. CALCIUM POLYSULFIDE BASELINE AND INJECTION PROCESS PERFORMANCE MONITORING.**

CaSx injection is generally implemented by either gravity feeding or pressure injecting into wells or borings. The specific injection plan should be site-specific and based on the results of the remedial investigation. Design factors such as the horizontal and vertical extent of the treatment zone, the mass of chromium to be treated, and any treatability or pilot study results for the CaSx treatment of chromium at the specific site should be considered. In general, the baseline and injection process performance monitoring should occur at the source area, mid plume, plume fringe, and sentinel well locations, although at least plume fringe and sentinel locations may not be necessary for short-term pilot tests. The baseline groundwater sampling event should be conducted as close to the initiation of the injection as possible. The parameters for monitoring are discussed below and listed in Table 5.

- Groundwater Field Parameters – Groundwater field parameters should include water level, temperature, specific conductance, pH, ORP, and DO. Water level measurements should be conducted at all available monitoring locations to evaluate the overall groundwater flow conditions during the injection, as well as to evaluate potential

groundwater mounding during the injection process. The pH, ORP, and DO parameters are of particular importance with respect to CaSx injection, as they are direct indicators that conditions for Cr<sup>VI+</sup> conversion to Cr<sup>III+</sup> are being created (i.e., slightly basic pH, elevated ORP, and reduced DO). Groundwater field parameters should be measured at multiple equally spaced time intervals throughout the injection process.

- Groundwater Laboratory Analytical Parameters – The groundwater laboratory analytical parameters should include total Cr, Cr<sup>VI+</sup>, manganese (Mn) iron (Fe), hardness (as CaCO<sub>3</sub>), TDS, Sulfide and Sulfate. Include arsenic also if it could be present naturally or from other sources (e.g., historic fill, pesticides, wood preservation, etc.), see Table 5.

#### **6.3.6.1.2. CALCIUM POLYSULFIDE REMEDIATION EFFECTIVENESS PERFORMANCE MONITORING**

The scope of the remediation performance monitoring will vary depending on site conditions and the size and scope of the remediation. The performance monitoring should be customized for the specific site hydrogeologic conditions; specifically, the monitoring events should be timed such that there is sufficient time for the CaSx to reach the treatment area and for the treated volume of groundwater to reach the down-gradient monitoring locations. Four to eight quarterly sampling events should be considered in order to account for potential seasonal variations. After the calcium polysulfide is consumed, additional monitoring may be necessary if MNA is considered part of the remedy. In general, it is recommended that the performance monitoring be conducted at the same locations as the baseline event. Groundwater field parameter data and measurements to be acquired should include water level, temperature, specific conductance, pH, ORP, and DO. Groundwater laboratory analytical parameters should include total Cr, Cr<sup>VI+</sup>, Mn, Fe, Hardness, TDS, sulfide, and sulfate. In formations consisting of glauconitic sands, silts and/or clays or where anthropogenic sources of arsenic may be present, arsenic should be monitored in order to determine if it is remobilized due to the CaSx injection. Increased sulfate concentrations can result in degradation of local concrete structures, including building foundations and monitoring well grout. The effects of the CaSx injection on local sulfate concentrations should be evaluated during the pilot study, and if necessary, the overall injection program should be modified to minimize the potential for sulfate degradation of concrete structures. Furthermore, if exceedances of the ground water quality criteria (GWQC) are expected for Mn, Fe, Hardness, TDS, sulfide, and sulfate as a result of the injection, then these exceedances should be addressed in the DGW Proposal for the PBR and/or groundwater CEA for original site contaminants. See Table 5 for a summary of monitoring parameters for all media.

#### **6.3.6.2. ZERO VALENT IRON (ZVI) INJECTION FOR THE TREATMENT OF CHLORINATED SOLVENTS**

Several applications of zero valent metals, including zero valent zinc, iron, nickel, and others have been developed for the treatment of chlorinated solvents and other contaminants in

groundwater. However, due to factors such as cost and availability, the most commonly utilized metal is zero valent iron (ZVI). Therefore, this section focuses on the application of ZVI relative to the treatment of chlorinated volatile organic compounds (CVOCs). In this technology, the ZVI is oxidized in the subsurface, creating reducing conditions that chemically degrade CVOCs.

Relatively quick and substantial reductions of CVOCs can ensue. ZVI typically persists in the subsurface for a duration of 5 to 10 years, thus creating a long term treatment zone. The reducing conditions that remain in the aquifer are an added benefit of this technology and may induce biological activity, creating an active natural attenuation zone that migrates with ground water. The reactions involve the oxidation of the ZVI, which in the aqueous environment results in the production of free electrons and hydrogen ions. The free electrons and hydrogen ions are then involved in a reduction reaction wherein the contaminant's chlorine ions are replaced by the hydrogen ions, consuming the excess electrons in the process.

This chemical process can be emplaced in a variety of settings using nano-scale to granular scale iron particles, including iron filing PRBs, funnel and gate PRBs, direct injection, etc. PRBs are dependent on the dissolution and transport of CVOCs through the barrier. Their effectiveness is highly dependent on the local hydrogeology and design of the PRB. The long term performance of the PRB is dependent on ground water geochemistry and the potential for clogging, which may result in the plume bypassing the barrier. Direct injection of nano-scale or micro-scale ZVI into the source area and down-gradient plume can also reduce the cleanup time, and this approach is less dependent on local hydrogeologic gradients to carry the contaminants through a treatment zone. Emplacement of ZVI in the subsurface requires a NJPDES permit-by-rule.

While injection of nano-scale ZVI can be conducted via injection wells/points, micro-scale ZVI injection is generally implemented by injection into borings. This approach avoids the potential problems of clogging of the well screen and filter pack, which commonly occur when injecting a micro-scale ZVI slurry via permanent injection wells.

#### **6.3.6.2.1. ZVI INJECTION PROCESS PERFORMANCE MONITORING**

Factors such as the horizontal and vertical extent of the treatment zone, the mass of CVOCs to be treated, and any treatability or pilot study results should be incorporated into the final design of the remedy. In general, the injection process monitoring should occur at the same locations as the long-term performance monitoring. Injection process monitoring should include a baseline groundwater sampling event, which should be conducted as close to the initiation of the injection as possible. The baseline event field parameters should include depth to water (and the associated water level elevations), DO, ORP, temperature, pH, and specific conductivity. Note that pH is a critical indicator that dechlorination is occurring as these reactions typically release  $\text{OH}^-$  and pH should increase as the reactions occur. All laboratory samples should be analyzed for CVOCs, iron (both field filtered and total), alkalinity, total dissolved solids (TDS), and chemical oxidation demand (COD). Furthermore, acetylene is a byproduct of abiotic

dechlorination of PCE and TCE, thus monitoring for acetylene may be beneficial in demonstrating that abiotic dechlorination is occurring; however, acetylene is unstable and readily converts to ethene. In order to evaluate the potential for simultaneous CVOCs reduction via in-situ microorganisms, evaluation of in-situ microbial populations should be conducted. The analysis of groundwater samples for the presence of microorganisms such as *Dehalococcoides etheneges* (DHC), the bacteria strain that will help to degrade the critical PCE degradation daughter products cis-1,2, -DCE and vinyl chloride, is recommended. The geochemical, hydrogeologic, and microbial data should be used to both characterize pre-installation chemical characteristics and hydrogeologic conditions to ensure that the ZVI is installed at the proper locations and that the impacted groundwater does not bypass the treatment zone.

During the injection process, detailed logs should be maintained to document the mass of ZVI injection at each injection point and vertical injection interval. Detailed observations of any ZVI “daylighting” should be made, and corrective actions should be taken if necessary to minimize the amount of daylighting. In particular, proper grouting of all injection borings should be completed before injection at new locations in order to minimize the potential for short circuiting and daylighting through previous borings. Water level measurements should be made at regular intervals to document any mounding effect created by the injection process. If possible, grab samples for iron analysis (both field filtered and total) should be collected at key observation points in order to document the distribution of iron in the subsurface.

As indicated in Table 7 below the monitoring plan should include any other media as appropriate based on site-specific conditions; this could include potential vapor intrusion into nearby structures due to physical displacement of vapors near the treatment zone.

#### **6.3.6.2.2. ZVI REMEDIATION EFFECTIVENESS PERFORMANCE MONITORING**

In general, it is recommended that the effectiveness monitoring be conducted for a duration and frequency that takes into account local seasonal hydrogeologic variations. In general, a total of eight quarterly rounds of sampling are recommended; however, this scheme may be modified based on local hydrogeologic conditions. Effectiveness monitoring should be conducted at the same locations as the baseline groundwater sampling event in order to monitor the progress of the remediation over two or more annual seasonal cycles. Groundwater field parameters and laboratory analytical parameters should be the same as the baseline groundwater sampling event; i.e., depth to water (and the associated water level elevations), DO, ORP, temperature, pH, and specific conductivity. All laboratory samples should be analyzed for CVOCs, iron (both field filtered and total), alkalinity, TDS, and COD. As with other reduction technologies, elevated levels of methyl ethyl ketone (MEK) and acetone may be a byproduct at some sites; but these concentrations typically attenuate rapidly to background concentrations (Fowler et al., 2011) but these contaminants should be monitored to confirm this expected result. Final compliance monitoring should include a comparison of the CVOCs and total iron concentrations with the applicable remediation standard or goals.

### **6.3.6.3. EMULSIFIED VEGETABLE OIL (EVO) INJECTION**

Emulsified vegetable oil (EVO) is a long lasting carbon substrate that can maintain reducing conditions in the subsurface and can be used to extend the effectiveness of previously injected reagents used to enhance chemical reduction of contaminants. EVO is also commonly used to enhance or stimulate anaerobic bioremediation by creating reducing conditions. EVO for environmental clean-up, made from 60% vegetable oil and 40% vitamins, nutrients and a co-substrate of lactate, can promote anaerobic microbial activities and maintain reducing conditions for an extended period, often up to several years. EVO consists of microscopic droplets designed to stick to the pore spaces.

During the initial several months following the EVO injection, methane concentrations may increase due to the proliferation of methane-producing bacteria, which occurs when high levels of carbon substrate like EVO are introduced into the subsurface. Methane can be metabolized by many microbes to carbon dioxide under aerobic conditions in the vadose zone. To ensure the complete mitigation of any potential methane issue, injection of small amounts of commercially available methane inhibitors is recommended to retard the proliferation of methanogens.

In addition to the methane inhibitors, lactate is often added as a readily digested and metabolized co-substrate. Lactate serves to substantially increase the microbial population early in the remediation process. Once the microbial population reaches a critical mass and the lactate is consumed, the microbes adapt to metabolizing the EVO as a longer lasting food source.

#### **6.3.6.3.1. EVO INJECTION PROCESS PERFORMANCE MONITORING**

Injection process monitoring includes a baseline groundwater sampling event that should be conducted at least two weeks prior to the injection. The baseline groundwater sampling event should be conducted at the same locations as the proposed remediation monitoring locations, which should include plume source, mid-plume, plume fringe, and sentinel wells as described in Section 5.4. The baseline event parameters should include the contaminants of concern (i.e., CVOCs, etc.), iron, manganese, nitrate, nitrite, sulfate, sulfide, methane, alkalinity, TOC, and TDS. Field parameters include depth to water (and the associated water level elevations), DO, ORP, temperature, pH, and specific conductivity.

#### **6.3.6.3.2. EVO EFFECTIVENESS PERFORMANCE MONITORING**

As with ZVI and CaSx, a specific performance monitoring program may be developed based on site-specific hydrogeologic conditions; however, quarterly monitoring for up to two years is recommended. The performance monitoring should be conducted at the same wells as the baseline sampling event. The analytical parameters will include the contaminants of concern, iron, manganese, nitrate, nitrite, sulfate, sulfide, methane, alkalinity, TDS, and TOC, depth to water (and the associated water level elevations), DO, ORP, temperature, pH, and specific

conductivity. Methane gas should be measured using a field detector at all the monitoring well heads and inside of any nearby building structures during each groundwater sampling events. As with other reduction technologies, elevated concentrations of methyl ethyl ketone (MEK) and acetone may be a byproduct at some sites; but these concentrations typically attenuate rapidly to background concentrations (Fowler, et. al, 2011), but these contaminants should be monitored to confirm this expected result.

Table 7. Performance monitoring parameters for chemical reduction technologies

| Sampling Media / Parameters  | In-Situ Chemical Reduction |                     |                          |
|--|----------------------------|---------------------|--------------------------|
|  | Zero Valent Iron           | Calcium Polysulfide | Emulsified Vegetable Oil |
| <b>Field Parameters<sup>+</sup></b>  |                            |                     |                          |
| pH*  | *                          | *                   | *                        |
| Dissolved oxygen*  | *                          | *                   | *                        |
| Oxidation-reduction potential*   | *                          | *                   | *                        |
| Temperature*   | *                          | *                   | *                        |
| Conductivity*  | *                          | *                   | *                        |
| Ferrous iron   | 3                          | 3                   | 2                        |
| Reducing Agent (a)   | 2                          | 2                   | 4                        |
| Non-Aqueous Phase Liquid (NAPL) monitoring   | 3                          | 3                   | 3                        |
| Depth to water*  | *                          | *                   | *                        |
| Depth of well*   | *                          | *                   | *                        |
| <b>Lab Parameters - Ground Water</b>   |                            |                     |                          |
| Volatile organic compounds (VOCs)  | 3                          | 3                   | 3                        |
| Sampling Media / Parameters  | Zero Valent Iron           | Calcium Polysulfide | Emulsified Vegetable Oil |
| Alkalinity   | 2                          | 2                   | 2                        |
| Nitrate-nitrite nitrogen   | 3                          | 3                   | 2                        |
| Fluoride   | 3                          | 3                   | 4                        |
| Total iron   | 2                          | 2                   | 2                        |
| Dissolved iron   | 2                          | 2                   | 2                        |
| Total metals (b)   | 3                          | 3                   | 3                        |
| Dissolved metals   | 3                          | 3                   | 3                        |
| Sulfate  | 2                          | 2                   | 2                        |
| Dissolved ethene, ethane, and methane  | 2                          | 3                   | 2                        |
| Total organic carbon (TOC)   | 2                          | 2                   | 2                        |
| Total Dissolved Solids (TDS)   | 2                          | 2                   | 3                        |
| Chloride   | 3                          | 3                   | 3                        |
| Bromide (or other tracer) (a)  | 3                          | 3                   | 4                        |
| Major cations (c)  | 3                          | 3                   | 4                        |
| Molecular biology assays (d)   | 4                          | 4                   | 3                        |
| Compound specific isotopic analysis  | 3                          | 3                   | 3                        |
| <b>Lab Parameters - Soil</b>   |                            |                     |                          |
| Contaminants and breakdown products  | 3                          | 3                   | 3                        |
| Fraction organic carbon  | 3                          | 3                   | 3                        |
| Total metals (b)   | 3                          | 3                   | 3                        |
| Total iron   | 3                          | 3                   | 3                        |
| <b>Other Media</b>   |                            |                     |                          |
| Vapor intrusion sampling for site or technology specific contaminants  | 3                          | 3                   | 3                        |
| Surface water, sediment, pore water sampling for site or technology specific contaminants or secondary impacts | 3                          | 3                   | 3                        |

Notes: See Section 5.4 for a detailed discussion of notes 1, 2, and 3 below.

+ - For Field Parameters see Appendix B

\* - Standard field parameters required for all ground water sampling events

1 - DGW Required analysis

2 - Recommended analysis

3 - Conditional analysis

4 - Analysis not applicable

- (a) Injectant indicators and tracers vary by technology. These may include field colorimetric indicators and/or shake testing (see Appendix B) for soil flushing agents, field and/or laboratory analysis of helium for air sparge helium tracers, laboratory analysis of indicators for soil flushing agents, etc.
- (b) Total Metals - based on results of initial investigation (see Section 6.3.5.8.1)
- (c) Includes calcium, manganese, magnesium, sodium, and potassium
- (d) Includes Phospholipid Fatty Acids (PLFA), CENSES, and QuantArray

## 6.4. THERMAL PROCESSES

The in situ thermal (IST) processes discussed below involve heating the subsurface to volatilize organic compounds. The vapor phase compounds then migrate to the vadose zone where a vapor recovery system collects the gases with subsequent treatment at the surface, usually with granular activated carbon or oxidizers. An evaluation of the USEPA CLU-IN Database revealed that the most commonly applied IST technologies used were electrical resistance heating (ERH), followed by steam-enhanced extraction (SEE), and then thermal conduction heating (TCH). TCH, however, was used slightly more often than SEE since the year 2000 (Triplett Kingston et al., 2010). The performance monitoring guidance in this document will focus mainly on ERH and TCH, since they are used most often, but SEE is also addressed. Less commonly used thermal technologies, including vitrification and micro-wave heating, are not further specifically discussed.

Thermal technologies are appropriate for the treatment of petroleum hydrocarbons, chlorinated solvents, 1,4-dioxane, pesticides, NAPLs, coal tars, PCBs and dioxins. Design considerations include making sure adequate energy sources are available and that any manmade structures, above or below the surface, can withstand elevated temperatures.

Thermal treatment is well suited for NAPL remediation, as the vast majority of VOCs and SVOCs form positive heteroazeotropes, meaning they will boil in the presence of water (or moisture) at temperatures below the boiling point of water. Continued heating of the subsurface boils off the dissolved and sorbed-phase contaminants, mobilizing them for recovery by vacuum extraction. Thermally enhanced volatilization at temperatures well below the boiling point of the COCs can also be a significant removal mechanism.

In addition to the process of steam distillation, recovery and treatment of VOCs, the following other heat related impacts may further enhance in situ remediation mechanisms (USEPA 2014; USACE 2014; Triplett Kingston et al., 2010):

- increased biotic and abiotic reaction rates;

- dramatic increases in dissolved organic carbon concentrations, usually monitored as TOC, due to the hydrolysis of naturally deposited fulvic and humic acids (hydrolysis is an abiotic process greatly affected by elevated temperatures);
- increased mass transfer of residual NAPL to the aqueous phase, where biodegradation occurs; and
- lowering the viscosity of long-chain hydrocarbons. Thermal applications do not typically include heat-enhanced remediation of large dissolved-phase plumes due to cost considerations; however, monitoring data from multiple sites indicates increasing ground water temperatures increases dissolved organic carbon levels and may increase biodegradation rates (Triplett Kingston et al., 2010). Case study data appears to indicate this can help ensure that enhanced reductive dechlorination then becomes a more cost effective polishing technology as a result (USEPA 2014).

Additional considerations are potential formation of highly corrosive conditions and the electrical energy required. For example, if concentrated halogenated organics are the contaminants of concern, the piping and treatment system must be designed to withstand highly corrosive conditions (USEPA 2004; USEPA 2006; Baker and Heron 2004).

Design and monitoring considerations include the heat range of the monitoring equipment, management of vapors produced or mobilized, soil type, moisture content, presence of NAPL, all locations or media where mobilized contaminants might escape recovery efforts or impact receptors and the potential for surface voltages (i.e., measuring voltages on the surface of any potentially affected structures). Section 6.4.4 includes some suggested performance monitoring procedures for the thermal processes discussed below and references for more detailed monitoring information.

#### **6.4.1. ELECTRICAL RESISTANCE HEATING**

ERH involves conditioning readily available alternating current (AC) so that electricity flows throughout the subsurface matrix among an array of subsurface electrodes. The resistance of the subsurface materials to the flow of electricity produces heat, eventually reaching the boiling point of water. The produced steam carries the gas phase contaminants to the vadose zone, where a vapor recovery system collects and treats the vapors. The technology works equally well in the vadose and saturated zones. Although silts and clays typically conduct electricity more efficiently, ERH can work just as well in high permeability systems, such as sand and gravel, as in low permeability systems of bedrock or predominately silts and clay, but is less efficient in materials with high organic content.

To optimize performance, the subsurface media adjacent to the electrodes should remain sufficiently moist, which allows the flow of electricity (USEPA 2004). Discharges to the ground for this purpose require a NJPDES Permit-by-Rule if the source water used is potentially

contaminated. Please refer to Section 6.4.4 below and Section 7.1 for applicable permit requirements.

A key design metric is energy density. Increasing energy density increases contaminant removal efficiency. Increasing the power to the electrodes, or the number of electrodes within a given treatment volume, increases energy density. Horizontal spacing between electrodes is typically from 14 to 24 feet. Sites usually reach boiling temperatures in about six weeks and typical remediation time frames range from three to nine months, depending on the contaminants of concern, treatment volume and goal and objectives.

Practitioners generally apply ERH to remediate VOCs. While ERH can work for less volatile compounds, the cost may become prohibitive, as energy costs increase for less volatile contaminants.

As it requires water (or moisture) in the matrix to conduct electricity, ERH, by necessity, should not cause subsurface desiccation and any resulting negative effect where significant impacts on soil stability must be prevented.

ERH generates relatively uniform temperatures in the subsurface that are easily controlled. It can be used to create temperatures throughout the matrix that can enhance volatilization, bioremediation kinetics, iron reductive dehalogenation or the hydrolysis of pesticides and energetic compounds (explosives). The cost to achieve and maintain these uniform, relatively low temperatures, as compared to boiling temperatures, should be less and vapor capture may not be necessary where vapor intrusion will not occur or where VI mitigation systems are already in place to protect receptors. This approach may help achieve a plume-wide solution in much less time than would be required at ambient temperatures.

#### **6.4.2. THERMAL CONDUCTION HEATING**

TCH, which operates best in unsaturated soil, generally uses vertical heater/vacuum wells. A typical array consists of six heater wells in a hexagonal pattern with a heater vacuum well in the center of each hexagon, although it is feasible to use only combined heater/vacuum wells for the entire well array. For very shallow treatment areas within about six inches of the ground surface, surface heater blankets may be appropriate.

When not using a heater blanket, the method involves heating the wells, usually with electricity, to many hundreds of degrees Celsius. Heat conducts away from heater wells through earth materials, which have rather uniform thermal conductivity properties. For this reason, in part, the system designer can predict the rate the heat front expands with relative accuracy; this rate is used in determining heater wells spacing (USACE 2014).

Because TCH can achieve such high temperatures, it may be more appropriate for remediation of SVOCs in the vadose zone. Because the heater wells are so hot however, parts of the matrix will

desiccate, which will affect the weight-bearing loads of the soil. Desiccation can shrink and crack the soil, which could facilitate the removal of organics contained within them. Remediation of SVOCs, including high boiling point compounds such as PAHs or PCBs, generally requires soil temperatures of 325°C for adequate desorption. The increase in vapor pressure during heating allows for the treatment of high-boiling point contaminants at temperatures well below their boiling points. Closer well spacing may decrease the time required to reach design temperatures.

Some remediation professionals have applied TCH to remediate saturated soil with low hydraulic conductivity. Heating around the TCH well creates a dry zone in the immediate vicinity for vapor capture. Sustained heating boils off any water that migrates into the dry zone. In high permeability saturated soil, the influx of water into the dry zone may quench the soil, preventing it from exceeding the boiling point of water and achieving target temperatures.

#### **6.4.3. STEAM ENHANCED EXTRACTION**

Steam enhanced extraction (SEE) involves injection of steam into wells and the extraction of heated groundwater, contaminants, and vapor from the recovery wells, which are piped to a treatment system and/or containerized for offsite disposal. SEE systems are typically designed using an “outside-in” approach, where the contaminated zone is surrounded with steam injection wells, and contaminants are recovered from the central extraction well. Initially, steam injected into the subsurface loses its latent heat of vaporization to the soil, condensing into a hot water phase that moves radially away from the injection well, displacing air and water as it moves forward. Continued steam injection heats the soil in the vicinity of the well to steam temperatures, which along with the steam pressure further propagates the steam/hot water front. However, the migration of steam, water, and contaminants will tend to migrate in the more permeable zones.

Hot water/steam volatilizes contaminants sorbed to soils and reduces the viscosity of NAPL, enhancing contaminant mobility, which can aid recovery. However, volatilized compounds at the leading edge of the steam zone may condense, forming a contaminant condensate bank, which, depending on the type of contaminants present, may sink. Proper placement of the recovery well is essential to capture this contamination and performance monitoring below the treatment zone may be warranted.

#### **6.4.4. PERFORMANCE MONITORING FOR IN SITU THERMAL PROCESSES:**

The primary performance parameter is the reduction in concentration of the contaminants of concern in a manner that minimally impacts any potential receptors. Performance parameters, frequencies, and reasons for monitoring various media, and New Jersey specific requirements are briefly discussed below. See recent U.S. Environmental Protection Agency (USEPA) and U.S.

Army Corps of Engineers (USACE) in situ thermal remediation guidance documents (USEPA 2014; USACE 2014) for detailed monitoring recommendations.

#### **6.4.4.1. PROCESS MONITORING**

For ERH or TCH to be effective, the treatment zone must reach and hold appropriate temperatures. Thermal remediation vendors routinely monitor and record temperatures throughout the treatment zone, usually using thermocouples. Temperature monitoring points should be located in the treatment zone at the locations that will take the most time to heat up. More frequent monitoring of water levels during ERH operation and monitoring soil moisture content during TCH may be useful for optimizing or evaluating the heating process.

Pre-treatment influent vapor and aqueous phase sampling is recommended to determine the amount of contaminants removed. Vapor effluent streams can vary significantly over short periods of time, therefore direct reading instruments (e.g., handheld Flame Ionization Detectors) can be used for optimization purposes.

Contaminants in soil vapor can be measured at the vapor treatment influent header to evaluate system performance and to determine when the system can be shut down to begin the post remediation performance monitoring phase, such as when influent concentrations drop below a predetermined level and remain there. If condensate is produced, it can be tested for contaminants and their potential byproducts to assist in mass removal calculations.

Discharge of any condensate back to the ground requires approval via a NJPDES permit-by-rule; however, discharge monitoring requirements are minimal in most scenarios as long as the treatment process is operating and the condensate is discharged only into the area undergoing treatment. Monitoring included in the RAW is expected to be sufficient without additional discharge monitoring requirements.

For SEE, the movement of the steam injection front in the subsurface should be tracked with temperature measurements along the steam path between the injection wells and the extraction wells. This may be supplemented with other technologies if appropriate. Pressure monitors are also useful to help ensure vapor and hydraulic control of the remediation.

The monitoring plan should include procedures for monitoring all nearby subsurface structures and neighboring civil infrastructure, such as utilities, tanks, buildings, basements, etc. for surface voltages, fugitive vapors or increased vapor intrusion risk, unintended heating, etc.

#### **6.4.4.2. EFFECTIVENESS MONITORING**

Applicable baseline ground water and/or soil data should be available, or collected, prior to operating the system. Ground water, soil and/or vapor samples can be collected at any time during the remedial process to monitor performance progress, however care must be used to

follow standard operating procedures for safe handling of hot liquids, hot soils, or hot condensing vapors (USACE 2014; IDEM 2010) where there is any risk of elevated temperatures. The overall success of the remediation should be evaluated after all thermal units have ceased operation by collecting soil and ground water samples throughout the treatment zone, specifically targeting source and plume fringe areas. Monitoring ground water and vapor intrusion risk until, or after, ground water temperatures return to pre-treatment conditions may be necessary to evaluate overall treatment effectiveness if contaminants still exceed standards at that time and/or if elevated temperatures produce or threaten to cause any negative impacts on existing ground water uses, on surface water quality, or due to enhanced vapor migration.

Effectiveness monitoring of ground water monitoring wells should also be conducted to verify control of contaminant migration. This should include measuring piezometric levels (manually or with transducers) and collecting samples for laboratory analysis of contaminant concentrations. Initially, a weekly monitoring frequency for the first month may be appropriate, followed by monthly monitoring during operation of the treatment system. A comparison of mass recovery rate vs. energy input is a key performance indicator for evaluating system efficiency. Mass flux analyses can also be useful. Monitoring frequency can be adjusted depending on the results.

The investigator should have a thorough understanding of the degradation products of the contaminants of concern and the current CSM for the site to develop an effective monitoring program. For example, for some chlorinated ethenes, ethanes and methanes, analysis of chloride concentrations in addition to the parent VO compounds can assist in mass removal calculations, especially when evaluating if applying electrical resistance heating enhanced to enhance biodegradation kinetics of the contaminants. Further, elevated temperatures can increase the rate of hydrolysis of many halogenated alkanes, pesticides and energetic compounds (e.g., explosives). High levels of methyl ethyl ketone (MEK) and acetone may be a byproduct at some sites, but these concentrations typically attenuate rapidly to background concentrations (Fowler, et. al, 2011), however these contaminants should be monitored to confirm this expected result.

If part of the overall site remedial objective is to directly enhance in situ remediation of the dissolved plume via some of the other heat related mechanisms listed above, ground water TOC concentrations may be an important appropriate indicator parameter. In that case, TOC monitoring pre-treatment and again when ground water temperatures are expected to be near maximum levels may provide useful information for evaluating the effectiveness of the thermal technology regarding that objective.

Table 8. Performance monitoring parameters for thermal technologies

| Parameters   | In-Situ Thermal Treatment |
|--|---------------------------|
| <b>General - Field Parameters+</b>   |                           |
| Depth to water*  | *                         |
| Depth of well*   | *                         |
| NAPL Thickness   | 2                         |
| Temperature in monitoring network  | 2                         |
| Pressure in monitoring network   | 2                         |
| Soil Moisture (for TCH)  | 2                         |
| Volume of Drip Water (Recirculated Condensate)   | 1                         |
| Energy Input   | 2                         |
| Surface Voltages   | 2                         |
| Extraction Flow Rate   | 2                         |
| Extraction Total Volume  | 2                         |
| Extraction Pressure / Vacuum   | 2                         |
| Vapor Extraction Concentration   | 2                         |
| Monitor nearby buildings, subsurface structures, etc. (e.g., vapors, heat, measuring surface voltages) | 2                         |
| pH*  | *                         |
| Dissolved oxygen*  | *                         |
| Oxidation-reduction potential*   | *                         |
| Temperature*   | *                         |
| Conductivity*  | *                         |
| <b>Groundwater - Lab Parameters</b>  |                           |
| Contaminants and breakdown products  | 2                         |
| Total organic carbon   | 3                         |
| Alkalinity   | 3                         |
| Chloride   | 3                         |
| Ferrous Iron   | 3                         |
| Nitrate  | 3                         |
| Sulfate  | 3                         |
| <b>Soil - Lab Parameters</b>   |                           |
| Contaminants and breakdown (BD) products   | 2                         |
| <b>Soil Vapor - Field Parameters</b>   |                           |
| Contaminants / BD Products (Headspace)   | 2                         |
| Extraction Pressure / Vacuum   | 2                         |
| <b>Soil Vapor - Lab Parameters</b>   |                           |
| Contaminants / BD Products (Headspace)   | 2                         |
| Contaminants / BD Products (Extracted)   | 2                         |

Notes: See Section 5.4 for a detailed discussion of notes 1, 2, and 3 below

+ - For Field Parameters see Appendix B

\* - Standard field parameters required for all ground water sampling events

1 - DGW Required Analysis

2 - Recommended analysis

3 - Conditional analysis

4 - Analysis not applicable

## 7. PERMITTING

The focus of this document is to provide technical guidance on the performance monitoring of in situ remedial actions. However, since in situ remedial actions frequently involve discharging a reagent or discharges of other substances, it was deemed appropriate to include some related information on the NJPDES permit-by-rule (PBR) used by SRP and the associated DGW proposal.

Additionally, this section briefly discusses other types of permits, approvals, etc. that the investigator may need to address when implementing an in situ remedial action, including requirements applicable in the Pinelands and in the Highlands Region and remedial action permits issued under the ARRCs rules.

### 7.1. THE SRP PERMIT-BY-RULE AT N.J.A.C. 7:14A-7.5

Before proceeding with remediation subject to the NJPDES rules, the investigator should be familiar with the NJPDES Discharges to Ground Water Technical Manual for the Site Remediation Program (or an updated version of this manual) at <http://www.nj.gov/dep/srp/guidance/njpdes/> and the applicable NJPDES rules, N.J.A.C. 7:14A at <http://www.state.nj.us/dep/dwq/714a.htm>. Some type of NJPDES permit is required to conduct almost all discharges to ground water (DGWs) in New Jersey. DGWs regulated by the SRP via a PBR include, but are not limited to:

- the injection of fluids, or release to the ground of other substances containing pollutants, as part of an in situ remedial technology for treatment of soil or ground water contamination;
- a discharge of recovered ground water that is part of site remediation or that occurs as a result of a dewatering project at any contaminated site or at a regulated underground storage tank facility; or
- any other actual or potential discharge of pollutants into, or onto, the ground, designed to occur at a contaminated site as part of any phase or stage of remediation.

SRP has generally not used a NJPDES permit to regulate the injection of pure oxygen (not ozone) or unpolluted atmospheric air that is part of a remedial action. The same is true for injection of heated water from a potable source. Both those types of injections are however subject to the general and specific remedial action requirements, N.J.A.C. 7:26E-5.1 and 5.2, which include: protecting public health and safety and the environment; not causing an uncontrolled transfer of contaminants from one medium to another nor a natural resource injury; and preventing further exposure of any receptor to any residual contamination. As previously indicated in Section 5 above and per N.J.A.C. 7:26E-5.5(b)6 and 7, monitoring of such remedial actions must document

compliance with these requirements based on all risks potentially posed by them (e.g., contaminant displacement, vapor intrusion, explosive hazards, surface water impacts).

Injection or other discharges of recovered groundwater from the contaminated site, discharges of steam generated from it, or condensate of such ground water would usually be regulated via a PBR. See the above referenced NJPDES DGW technical manual for more detailed information.

The NJPDES PBR definition states that PBR “means a provision of this chapter stating that a “facility or activity” is deemed to have a NJPDES permit if it meets the requirements of the applicable regulations.”

Note that while they are analogous, the DGW proposal is not a NJPDES permit application and the Department’s written approval letter is not, by itself, a NJPDES permit.

A DGW proposal and a RAW are separate documents; a DGW proposal should not be submitted as part of a RAW. A DGW proposal may be submitted alone to implement an IRM, pilot test, design study, etc. or concurrently with a RAW for a remedial action that includes a discharge to ground water. When they are submitted at the same time, the Department’s PBR discharge approval (i.e., authorization) letter is not an approval of the RAW; it is only an approval of the DGW proposal.

N.J.A.C. 7:14A- 7.5(b)1 requires that implementation of the discharge comply with N.J.A.C. 7:26E-5.1 and 5.2, as well as 5.6. If the Department’s review of the proposal indicates it appears to be inconsistent with the general and specific remedial action requirements of N.J.A.C. 7:26E-5.1 and 5.2, the proposal should be revised or supplemented to be consistent with all requirements of N.J.A.C. 7:26E-5 applicable to the discharge. The following technical guidance is provided to promote submittal of discharge proposals that are consistent with the general and specific remedial action requirements as well as N.J.A.C. 7:26E-5.6.

Note that at LSRP lead sites and UHOT sites, the Bureau of Ground Water Pollution Abatement (BGWPA) currently issues all PBR authorization letters; at traditional oversight cases, the applicable Department lead bureau will coordinate review and approval of DGW proposals.

### **7.1.1. OVERVIEW OF DGW PROPOSAL CONTENT**

A brief discussion of the required content of the entire DGW proposal is included below; the entire content is covered in more detail in the “Instructions for the Discharge to Ground Water Permit-By-Rule Authorization Request” and in the NJPDES DGW technical manual.

N.J.A.C. 7:26E-5.6 requires each discharge to ground water proposal be submitted with a “Discharge to Ground Water (DGW) Permit-by-Rule Authorization Request” form. Any proposal submitted is required to contain or be submitted with the following components, as applicable:

1. A summary of the remedial investigation in and around the treatment area and any areas of concern that will or may be impacted by the discharge. To avoid delays in processing, the summary should include current and past conditions, as well as ground water elevation measurements, a well construction summary table, contour maps and ground water analytical data. Additionally, the investigator should indicate the extent and thickness of any free product in or near the discharge area and the extent of any residual product. Any available soils data in or near the treatment area should be provided. The summary should also identify and discuss any preferential pathways and nearby receptors. Submitting a copy of the entire remedial investigation report that includes the information listed above is also acceptable.
2. The chemical content of all fluids and substances to be discharged or placed into or onto the ground to implement the remedial action. The NJPDES rules, in Subchapter 4, list substances the Department considers pollutants, including the parameter list in Section 4.4(b)3.
3. The concentrations of all contaminants expected to be present in recovered ground water prior to treatment. Indicate whether collection of free product is expected.
4. The type, location, volume, and duration of the proposed discharge to ground water. If applicable, the anticipated extent of influence of the discharge should be indicated relative to the contaminant source area, the ground water monitoring locations and potential receptors. The maximum discharge duration that can now be permitted for any one DGW proposal is 5 years pursuant to N.J.A.C. 7:14A-2.7(a), as explained in the next to last paragraph of the webpage at <http://www.nj.gov/dep/srp/guidance/njpdes/>.
5. A discussion of the potential effect that the proposed discharge may have on ground water or any other receptor.
6. A detailed description of how the discharge to ground water would comply with the GWQS and SWQS (e.g., antidegradation policy, classification exception area (CEA) requirements, and N.J.A.C. 7:9C-1.2(b) and 1.7(g) regarding risk to surface waters, [http://www.nj.gov/dep/rules/rules/njac7\\_9c.pdf](http://www.nj.gov/dep/rules/rules/njac7_9c.pdf) ).
7. If applicable, a proposal for a “permit-related CEA” (see Appendix A of the SRP NJPDES DGW Permit Technical Manual) for the area where the permitted discharge will, or could, cause the GWQC to be exceeded outside of an existing CEA for the site or for constituents not included in any existing CEA, or otherwise outside of the area of contamination.
8. A monitoring plan, which is discussed in Section 7.1.2 below.
9. A public notice, if applicable. If the proposed discharge duration (not the monitoring duration) is going to exceed 180 calendar days from the initial date of discharge and the

discharge is not associated with a residential heating oil remediation, the investigator must follow all public notice requirements at N.J.A.C. 7:26E-5.6(c).

### **7.1.2. SPECIFIC TECHNICAL GUIDANCE FOR DGW PROPOSAL AND MONITORING PLAN**

Use both the general technical guidance of Section 5 above, and the applicable technology specific technical guidance in Section 6 above, to develop the monitoring plan for the DGW Proposal. The monitoring parameter tables in Section 6 list most of the technology specific recommendations for the monitoring parameters and should serve as a starting point for a site-specific parameter list. The monitoring plan should clearly identify the ground water sampling locations, well construction details, sampling depth interval(s), sampling parameters, sampling methodologies, and sampling frequency. Pursuant to N.J.A.C. 7:26E-5.6(b)5 and 8, N.J.A.C. 7:14A-7.1 and N.J.A.C. 7:9C, ground water sampling parameters must include the chemical constituents in the fluid to be discharged and any constituents that may cause ground water quality to contravene a numeric GWQS or SWQS criterion, or violate a narrative standard, as a direct or an indirect result of the discharge.

The monitoring plan should include sampling of other media as necessary to address risks to all potentially affected receptors (e.g., surface water, ground water, soil, indoor air).

The monitoring plan duration under the PBR should be specified; and it must be for a sufficient time to document whether the discharge has had any negative effects. Unless a PBR permit-related CEA (see Section 7.1.3) is in effect, the monitoring duration can be less than what is appropriate for monitoring of the performance of the remediation technology in treating or eliminating contaminants of concern (e.g., the monitoring duration in the RAW).

The monitoring plan should include discussion of contingency sampling for situations when exceedances caused by the discharge extend beyond the monitoring period stipulated in the DGW proposal. At a minimum, the contingency plan discussion should indicate that sampling will continue until two consecutive samples, taken long enough apart to account for seasonal fluctuations in ground water conditions indicate that there are no longer any exceedances.

The monitoring plan in the DGW proposal should indicate that additional sampling under the PBR is not required if comparison of baseline and post-treatment sampling results indicate the criteria were exceeded due to natural conditions, pre-treatment conditions or because of inappropriate sampling procedures, not as a result of the discharge. Note that natural or background conditions could also potentially be determined from nearby, un-impacted or upgradient wells if insufficient pre-injection data are available.

If the DGW proposal is submitted with or after a completed RIR, the investigator should include maps and narrative that describe the full horizontal and vertical extent of free and residual product and the extent of the dissolved plume. When a DGW proposal is submitted prior to completion of the RIR, the currently known extent of any free and residual product, and/or of the

dissolved plume, in the treatment area should be depicted. In either situation, the goal of the remedy that includes the DGW should be explained in the DGW proposal.

If treatment or removal of the product is the goal, the investigator should depict an anticipated treatment area that covers the full horizontal and vertical extent of free and residual product. Likewise, if treatment of a broader source area is the goal, such as soil contamination greater than the Remediation Standards, the horizontal and vertical extent of the contamination should be depicted, along with the zone of anticipated treatment, so that performance monitoring points can be appropriately placed.

If the objective of an in situ remedy that includes a DGW is containment of the source area, the extent of free and residual product should be depicted on a map, as well as any other contamination considered to represent source material. Performance monitoring points should be placed to demonstrate if containment has been achieved (i.e., if the actions limit or prevent uncontrolled discharges/spreading of contamination).

If containment of some or all dissolved contamination is the goal of a remedy that includes a DGW, performance monitoring points should be placed to demonstrate the dimensions of the capture zone. The dimensions of the area to be contained, or the capture zone for dissolved contamination, are needed to determine which, if any, discharge limits are applicable for a DGW. Refer to the NJPDES DGW technical manual for additional information regarding such DGW proposals.

Performance monitoring data points should be in, and immediately around, the anticipated treatment zone and along the migration pathways of the contaminant plume. The investigator should propose or install points as described in Sections 4 and 5 of this technical guidance, rather than attempting to rely on previously installed monitoring points that may have been installed for another purpose and don't adequately monitor the discharge.

In developing a monitoring plan to address any media or receptor potentially negatively impacted by the discharge, consider possible physical displacement of any subsurface contaminants by the discharge (in any phase or media), as well as technology specific impacts. For example, if a building is near the source area or the dissolved plume, a nearby discharge of any kind could physically displace vapors within the vadose zone, which may subsequently cause or exacerbate vapor intrusion into the nearby building. If free or residual product is, or may be, in close proximity to any structure, a nearby discharge could also displace product into or toward it during or after the discharge. In such situations, the monitoring plan must include appropriate vapor and/or visual monitoring commensurate with the degree of risk involved and the duration of the discharge. See the vapor monitoring in Section 5.4.3 for more information.

Pursuant to N.J.A.C. 7:26E-5.6(b)8 the DGW proposal must include a schedule for submission of sampling results.

### **7.1.3. NJPDES PERMIT-RELATED CEA**

Those preparing the DGW proposal should review the “In Situ Treatment Discharges” in Appendix A of the NJPDES DGW technical manual. It states in part “the amount and concentration of substances discharged should be the minimum levels that provide effective in situ treatment of subsurface contaminants.” The person responsible for conducting the remediation is responsible for any negative secondary impacts of an approved discharge and for performing any associated monitoring or other remediation necessary as a result of those impacts. With the following exception, if new, localized and/or temporary violations of the GWQS are expected, or are possible, due to the proposed discharge, the proposal should include a NJPDES permit-related CEA for those constituents, as discussed above in item 7 of Section 7.1.1. The exception is if those constituents, and the area to be impacted, are already included in a CEA established for the site plume pursuant to N.J.A.C 7:26C-7.3; in that case, a NJPDES permit-related CEA for them is not needed. Likely constituents for a permit-related CEA are:

- sulfate, sodium, iron, pH and hardness due to constituents included in various remediation products;
- newly produced cis 1,2 dichloroethene, vinyl chloride, acetone or methyl ethyl ketone due to enhanced reductive dechlorination or other mechanisms; and
- dissolution of naturally occurring iron or manganese in the formation due to changes in basic ground water chemistry (e.g., pH, dissolved oxygen, etc.).

Review Appendix A of the NJPDES DGW technical manual, Section I.A.1, for additional policy and regulatory information about the NJPDES permit-related CEA approach.

### **7.1.4. AVOIDING COMMON PITFALLS IN DGW PROPOSAL PREPARATION**

To help avoid common pitfalls that delay issuance of DGW approval letters, or result in proposals that are not approvable, the investigator should ensure that the following information is included:

- The objective of the discharge. The reviewer can more readily determine the appropriateness of the monitoring plan if they know the purpose of implementing the discharge. For example, different monitoring approaches may be appropriate depending on if the discharge is part of an IRM, a pilot study for a portion of a source area, for treatment of an entire source area, or for polishing of low levels of residual contamination.
- A specific duration for the discharge even if the discharge is associated with a homeowner heating oil remediation.

- Well location maps, ground water contour maps, and analytical data.
- Boring logs, well construction details and depth to water information. Copies of Monitoring Well Certification Forms A and B (<http://www.nj.gov/dep/srp/srra/forms/>) should be provided, or if those were previously submitted, a table summarizing well construction details should be included.
- The well purging and ground water sample collection method used for existing data and the methods intended for proposed sampling. For example, if a depth discrete well sampling method is chosen, state whether one ground water sample will be obtained for each five feet of saturated screen, consistent with the Field Sampling Procedures Manual, or whether vertical profiling was previously done, which may justify sampling only within a particular targeted depth interval. Bear in mind that injections may alter the vertical contaminant profile, therefore sampling from multiple depths may be appropriate. As indicated by the Department's Field Sampling Procedures Manual in Section 6.9.2.5.1.10 (<http://www.nj.gov/dep/srp/guidance/fspm/pdf/fsmp2005.pdf>), depth discrete sampling IS NOT recommended for sentinel wells with a saturated screen length greater than five feet, as there is uncertainty where the contaminant front will arrive in the well, unless the well is vertically profiled every sampling round.
- An adequate number of wells to monitor the discharge. This often entails the installation of wells to augment the existing monitoring well network or conducting the in-situ treatment immediately up-gradient of existing wells. The thought is that wells should be located immediately down-gradient of the treatment zone and wells should be specifically located to monitor whether the discharge may cause unintended migration of the contaminant plume or contaminant mass transfer from one medium to another.

In addition, the investigator should:

- Focus treatment on the contaminant plume, rather than specific contaminated wells.
- Propose a monitoring duration that is sufficient to document any negative effects related to the discharge. This means allowing sufficient time for the discharge to reach the most down-gradient sampling locations, before the sampling program is terminated.
- If there are proprietary formulations, disclose all the chemical constituents within those formulations. The specific chemical formulas, ratios, or percentages need not be disclosed. The Department handles proprietary information as specified in the ARRCS rules at N.J.A.C. 7:26C-15.3, [http://www.nj.gov/dep/rules/rules/njac7\\_26c.pdf](http://www.nj.gov/dep/rules/rules/njac7_26c.pdf).
- Propose to monitor for all chemical constituents being discharged and include existing subsurface chemical constituents that may potentially become elevated due to the discharge.

- Propose the appropriate vapor monitoring when a discharge may cause vapor issues for nearby residences or other structures.

#### **7.1.5. PERMIT-BY-RULE REPORTING AND COMPLIANCE**

Permit by rule reporting is fairly straight forward. Consistent with N.J.A.C. 7:14A-2.11(a) and 6.2(a)14, within 30 days of initiation of a discharge, notify the Department by email (the person listed at the end of the approval letter) of the start date of the discharge.

Further, report any malfunction resulting in non-compliance that may cause an acute effect on public health, safety or the environment. Examples of such malfunctions include unintended impacts to potable wells, irrigation wells, daylighting into a surface water body or basement sump, discharge of treated ground water at concentrations greater than established effluent limits, etc. This reporting should be done within 24 hours after the malfunction was first observed or detected. Initial reporting should be done by phone and email to the contact person listed at the end of the approval letter. The phone and email reporting should be followed by a written report within seven days later.

When a report needs to be submitted to document a malfunction, include details of the malfunction, what has been done or is planned to mitigate or alleviate the malfunction and if a new or revised CEA is needed as a result. The report should also provide a brief summary of the approved discharge, the date when the authorized discharge began, the date that the malfunction or non-compliance began or was first observed, and the status of any new or revised CEA (e.g., permit-related CEA or site plume CEA). If a report is required, the investigator should consult the NJPDES DGW technical manual (Appendix A) to ensure that the necessary information is provided. The report should be clearly titled “PBR Compliance Report”. It should be sent to the contact person listed at the end of the approval letter using the address provided within the header at the top of the approval letter.

Pursuant to N.J.A.C. 7:14A-7.5 and/or N.J.A.C. 7:14A-8.16(c) and (e), if non-compliance with the PBR is not sufficiently mitigated such that continuing the discharge is clearly inconsistent with applicable requirements of N.J.A.C. 7:26E-5.1 and 5.2, PBR authorization to discharge “automatically terminates.”

If the contingency compliance ground water sampling requirements were implemented due to unintended exceedances of the GWQC or an extended duration for a permit-related CEA, and the resulting monitoring data document a decreasing trend or stable concentrations for those contaminants (e.g., iron or sodium), they can potentially be included in the CEA package and monitoring plan for a ground water RAP application. See Section 7.3 below for additional RAP application requirements in this scenario. If a decreasing contaminant concentration trend is not evident for these constituents, the person responsible for conducting the remediation could conduct or propose additional remediation to reduce ground water concentrations (e.g., irrigation and/or discharges for pH adjustments in the impacted area, etc.).

All PBR monitoring data must be submitted with the remedial action report (RAR) for the site and/or as indicated in the PBR authorization letter.

For sites with a long term active discharge duration, (i.e., beyond approximately one year), submittal of annual monitoring reports may be appropriate. Such an alternate schedule for submission of monitoring results should be determined during review of the DGW proposal. The PBR authorization letter should document whether any interim monitoring reports (e.g., annual reports) must be submitted prior to when the RAR is due. For UHOT cases, any interim monitoring reports should be submitted to the BFO case manager. For LSRP lead and traditional oversight cases the PBR letter, or other correspondence, will indicate where to send any interim monitoring reports.

#### **7.1.6. MODIFICATIONS TO THE DGW PROPOSAL**

The Department may approve revisions to a previously approved DGW proposal without requiring submittal of a new PBR form and the associated fee if the changes to the discharge are relatively minor (e.g., reagent volume adjustments, additional injection events within the same total discharge duration). Submittal of a new form and fee are required when a new discharge is proposed or the monitoring plan needs to be significantly changed (e.g., changing reagent, changing injection zones).

Requests to extend the discharge duration of an existing approved discharge beyond 180 days, at non UHOT cases, usually requires submittal of a new form, fee and DGW proposal along with the required copy of a public notice. For UHOT cases, a new form, fee, and proposal is required when the permit expires at the specified duration or maximum extent of five years from the date of the approval letter. Any questions can be directed to the contact person provided at the end of the PBR authorization letter.

#### **7.2. OTHER PERMITTING OR SIMILAR REQUIREMENTS**

The person responsible for conducting the remediation must obtain all necessary permits, approvals or determinations. Use of this technical guidance does not relieve any person from complying with requirements or provisions imposed by any other Federal, State or local applicable statutes or regulations or obtaining any and all permits required by State, Federal or local statute or regulation. Other permits include but are not limited to the following:

- NJDEP well permits ([http://www.nj.gov/dep/watersupply/pw\\_permit.html](http://www.nj.gov/dep/watersupply/pw_permit.html) ) and water allocation permits ([http://www.nj.gov/dep/watersupply/a\\_allocat.html](http://www.nj.gov/dep/watersupply/a_allocat.html) )
- NJDEP Air Quality Permitting Program requirements (<http://www.nj.gov/dep/aqpp/> )

- NJ Pinelands (see permitting, applications, etc. <http://www.nj.gov/pinelands/appli/> and [http://www.nj.gov/dep/landuse/lu\\_pl.html](http://www.nj.gov/dep/landuse/lu_pl.html) ); and
- NJ Highlands Preservation Area requirements (see below).

**Air Quality Permitting:** Appendices K and L of the 2016 Vapor Intrusion Technical Guidance, at [http://www.nj.gov/dep/srp/guidance/vaporintrusion/vig\\_appendices.pdf](http://www.nj.gov/dep/srp/guidance/vaporintrusion/vig_appendices.pdf), contain air pollution control permitting information relevant to any potential air pollution source, although they were written for sub-slab depressurization systems.

**NJ Pinelands:** N.J.A.C. 7:26E-1.5(i) of the Technical Rules states that the person responsible for conducting the remediation must comply with the statutes and rules applicable to the Pinelands and lists remedial phase documents that must be sent to the Pinelands Commission.

N.J.A.C. 7:26E-5.6(c) states that the Pinelands Commission must be sent a copy of any DGW proposal for a discharge in the Pinelands with a duration exceeding 180 days.

The investigator should be aware of the Pinelands Comprehensive Management Plan (i.e., Pinelands CMP or rule), see <http://www.nj.gov/pinelands/cmp/CMP.pdf>. At N.J.A.C. 7:50-6.73(b), (c) or (d) [page 197 of the CMP] this rule indicates that the prohibitions regarding processing, discharging and use of hazardous or toxic substances in the Pinelands do not apply to activities permitted by State or Federal law. It further indicates, the Pinelands Rule shall not be construed to prohibit or constrain development or operation of a facility essential for the remediation of a contaminated site. Pinelands permits are required for “Development” in the Pinelands, the definition of which is at N.J.A.C. 7:50-2.11, on pages 21 and 22 of the Pinelands rule. Part VIII of the Management Plan addresses Water Quality.

The investigator should contact the Pinelands Commission with any questions regarding the need to apply for a development permit or other approvals. General and contact information is at <http://www.nj.gov/pinelands/index.shtml> and for application and development questions see [http://www.nj.gov/pinelands/home/contact/application\\_and\\_development.shtml](http://www.nj.gov/pinelands/home/contact/application_and_development.shtml). If a remedial action does require “development” in the Pinelands, Part V- Waiver of Strict Compliance with Provisions of the Comprehensive Management Plan, contains a waiver at N.J.A.C. 7:50-4.62(d)1iii.(2), which may apply to remedial actions.

**NJ Highlands:** Any site remediation related work or discharge proposed within the New Jersey Highlands Preservation Area is subject to the Highlands Water Protection and Planning Act, and the Highlands Water Protection and Planning Act Rules, N.J.A.C. 7:38–1 et seq., see [http://www.nj.gov/dep/rules/rules/njac7\\_38.pdf](http://www.nj.gov/dep/rules/rules/njac7_38.pdf). General and contact information for the Highlands is at <http://www.nj.gov/dep/landuse/highlands.html>. Although the act and rules include an exemption for the remediation of any contaminated site, at N.J.A.C. 7:38-2.3(a)15, they also require that the Department shall issue written determinations of whether a proposed activity is exempt pursuant to N.J.A.C. 7:38-1.1(c)2. Therefore, a person responsible for

conducting the remediation at a site in the Highlands must complete a Highlands Applicability Determination and Water Quality Management Consistency Determination form found under the Highlands Program forms tab at <http://www.nj.gov/dep/landuse/forms.html>. Section III of the form covers applying for a Highlands applicability determination for exemptions; the site remediation exemption portion is on page 11, item 15. The associated fee is explained on page 2 of the form.

**Security Considerations:** The use of certain compounds (e.g., large quantities of oxidants or fertilizers) at a site may require coordination with Homeland Security; contact information is at [www.dhs.gov/main-contact-us](http://www.dhs.gov/main-contact-us). It is also advisable that you communicate with your supplier regarding any security related requirements that may be applicable to the acquisition and handling of the chemical compounds to be used.

### **7.3. GROUND WATER REMEDIAL ACTION PERMITS**

Remedial action work plans and DGW proposals that include in situ remedies are typically submitted to the Department prior to, during, or at the conclusion of the remedial investigation phase. Treatment periods for these technologies are often relatively short-term, thus it is more common to complete them prior to submitting the RAR and an application for a ground water remedial action permit (GWRAP) per N.J.A.C. 7:26E-5.7(b)7.

The purpose of the GWRAP is to regulate the long-term operation, maintenance and performance monitoring of remedial actions after the RAR has been submitted. The person responsible for conducting the remediation submits a plan to the Department for the operation, maintenance and performance monitoring of a remedial action and the Department incorporates that plan into a remedial action permit. Performance monitoring is associated with either 1) MNA or 2) an active remediation. N.J.A.C. 7:26C-7.9(a)6 indicates that the Department may include other conditions in the RAP concerning the ground water remedial action besides those specified in N.J.A.C. 7:26C-7.9(a)1-5.

Any remedial action that includes a proposed discharge triggers the DGW Proposal and NJPDES PBR requirements discussed above; such discharges are not authorized by a GWRAP.

#### **7.3.1. PRIOR TO APPLYING FOR A GROUND WATER RAP**

N.J.A.C. 7:26C-7.5 includes permit application requirements for the two types of ground water RAPs. Consistent with N.J.A.C. 7:26E-5.1(e) and the Ground Water Remedial Action Permit Guidance, the source of ground water contamination should have been effectively removed or treated prior to applying for a GWRAP for MNA. Before applying for an active remediation GWRAP the source should have been removed, treated or contained.

N.J.A.C. 7:26C-7.6(b)2, the Instructions for the Remedial Action Permit Application – Ground Water, and the Ground Water RAP Guidance, all indicate that prior to submitting an application for a ground water RAP for MNA, the investigator must obtain adequate ground water data to demonstrate that this passive remedy is effective. As stated in the MNA Technical Guidance, “a minimum of eight rounds will typically be needed to demonstrate the applicability of MNA. Of these eight rounds, four consecutive quarterly ground water monitoring events are necessary to evaluate spatial and temporal distribution.” Prior to applying for a RAP for active ground water remediation, N.J.A.C. 7:26C-7.6(b)3 requires the person responsible for conducting the remediation to demonstrate that the remedial action is operational and functioning as designed.

The investigator would need to apply for a RAP for active remediation of ground water if an in situ remedy is not completed (e.g., injections still occurring) before the RAR submittal deadline. It may be appropriate however for the investigator to apply for a RAP for MNA when only performance monitoring of an in situ remedy would extend beyond the RAR submittal date; this is appropriate if a sufficient number of monitoring events (typically 8 quarters) have been performed following the completion of the in situ remedy and this data demonstrate that any reagents discharged have been essentially depleted and there are decreasing trends in contaminant concentrations.

As discussed in sections 7.1.1 (item 7), 7.1.2, 7.1.3 and 7.1.5 above, some constituents (e.g., sodium or iron) may have been included in a NJPDES permit-related CEA under the PBR authorization letter or they may have triggered the contingency ground water sampling requirements indicated in a PBR authorization letter. For constituents introduced by an approved DGW that are not hazardous substances, but that have a GWQC, or that impact another constituent with a GWQC (e.g., hardness or pH), a minimum of four rounds of ground water sampling data would be acceptable for documenting a decreasing trend. This data could be from only the well or wells associated with the in situ remedy that were negatively impacted by the approved discharge instead of all wells that monitor the entire CEA. Eight rounds of data, however, in all affected wells are preferable.

### **7.3.2. AFTER A GROUND WATER RAP IS ISSUED**

An investigator may determine that implementing an in situ remedial technology is appropriate after a RAP was issued. In this situation, the person responsible for conducting the remediation is expected to implement performance monitoring procedures based on the guidance in Sections 5 and 6 above regardless of whether that would entail a greater sampling frequency or other additional monitoring that is not included in the RAP monitoring plan.

For an MNA RAP, if the final remedial goal is still to complete the remedial action using MNA after a short-term in situ treatment is completed, the permittee must, pursuant to N.J.A.C 7:26C-7.7(a)lviii (general RAP conditions), report that additional remediation was conducted. The date in situ treatment is completed should also be reported. Include this information with each

Remedial Action Protectiveness / Biennial Certification Form – Ground Water and associated biennial report submitted after initiating the in situ treatment. The permittee should also include all monitoring results for the in situ remedial action in the biennial report submitted when the data first becomes available.

Discharges authorized under one 180 day duration PBR discharge approval letter, or other remedial actions of similar tenure, would be considered short term treatment to enhance the MNA remedial action and application for a RAP modification does not need to be submitted (i.e., N.J.A.C 7:26C-7.12(b)2 is not applied in this situation). If the treatment has adverse effects, such as negative changes to the ground water contaminant plume extent (e.g., significant plume displacement) or adding additional contaminants to the plume that are still present above standards when the next biennial evaluation is completed, the permittee is expected to submit a GWRAP application for modification and a CEA/WRA Fact Sheet Form to modify the CEA and RAP as required per N.J.A.C 7:26C-7.12(b)2. However, for nonhazardous pollutants introduced or impacted by an approved DGW (e.g., sodium or pH), a CEA/RAP modification may not be needed if: 1) monitoring data indicate the impacts are localized, no other receptors are impacted and concentration trends indicate levels are in the process of returning to pretreatment conditions; 2) monitoring of these constituents continues under the PBR and a permit-related CEA until levels meet GWQC or return to background conditions; and 3) data documenting the above conditions are submitted in each GWRAP biennial report due after the in situ treatment was initiated.

If the MNA remedial action is to be changed to long-term use of an active in situ remedial technology or a remedial action that includes engineering controls, a GWRAP modification application is required to change the GWRAP from MNA to active remediation.

In either case, the licensed site remediation professional, pursuant to N.J.S.A. 58:10B-14, should use this technical guidance to develop and implement an appropriate remedial action performance monitoring plan for any in situ remedial action performed.

## **8. REPORTING**

This section covers data evaluation and interpretation as well as when and how performance monitoring data should be submitted to the Department.

Performance monitoring data associated with in situ remedial actions are reported to the Department in the same manner and frequency as any other remedial action; they are submitted with the appropriate key document submissions, predominantly the RAR. Requirements implemented through the DGW permit-by-rule may trigger additional report submittals as was discussed in Section 7.1.5 above.

## **8.1. DATA EVALUATION AND INTERPRETATION**

Data evaluation and interpretation is a crucial step in determining the performance or status of the remedial action. For further reference, see the ITRC document, Ground Water Statistics and Monitoring Compliance (<http://www.itrcweb.org/gsmc-1/Content/Resources/GSMCPDF.pdf>). It is important that enough data be collected to have confidence that the plume dynamics are understood and that the monitoring period and frequency were sufficient to detect any potential concentration rebound. It is also important that the investigator be able to identify approximately when the active phase of an in situ remedy is complete (i.e., be able to identify when injected reagents have been depleted). If progressing to MNA, the first round of quarterly data used to document attenuation should be obtained after the in situ remedy is complete and the data demonstrate that reagents have been depleted.

If the in situ remedy did not meet the goals, additional remediation may be necessary. The CSM and the implemented remedy should be reviewed to identify issues.

If a goal of the in situ remedy is to remediate free or residual product and concentrations remain that are indicative of free or residual product, additional remediation is needed, unless revising the goal to containment is appropriate. The investigator is reminded that, consistent with N.J.A.C. 7:26E-5.1(e), treatment or removal of free and residual product is required to the extent practicable. If treatment or removal of free and/or residual product is not practicable, containment is required as part of a Technical Impracticability proposal. All efforts to treat or remove the free or residual product must be documented as part of the Technical Impracticability proposal, as a line of evidence for the appropriateness of a Technical Impracticability determination, pursuant to N.J.A.C. 7:26E-5.1(e).

## **8.2. PERFORMANCE MONITORING DATA PRESENTATION AND DISCUSSION IN KEY DOCUMENT SUBMITTALS**

Like any other remedy, when reporting results for an in situ remedial action, all relevant data should be presented. The general reporting requirements of N.J.A.C. 7:26E-1.6 guide data presentation and discussion for all key documents submitted. When supplying ground water data, the sampling method used for every sample and for each sampling round should be clearly documented (e.g., volume averaged purge and sample, low flow, passive diffusion bags, etc.). All ground water field sampling summary sheets, results of low flow vertical profiling, well logs, well construction information, soil boring logs, etc. should be included and clearly labeled.

For sites where interim remedial measures (IRMs) have been implemented, the site investigation, remedial investigation and remedial action reports (SIR, RIR and RAR) are to include a presentation and discussion of the IRM related information identified or collected per N.J.A.C. 7:26E-1.10(a)2. Pursuant to N.J.A.C. 7:26E-4.9(a)3 and 5.5(b)2, respectively the RIR and RAW must both include a description of any previously implemented IRM. Pursuant to N.J.A.C.

7:26E-5.5(b)4, a RAW must include the results of any bench scale, pilot test or design studies that were conducted for either an IRM or for the planned final site remedy.

All RAR requirements are listed at N.J.A.C. 7:26E-5.7. These include documentation of the following:

- a summary of the in situ remediation;
- the dates of discharge;
- the objective or goals of the remediation;
- identification of the location of the source area;
- identification of where the remediation occurred;
- the presence of free or residual product; if applicable, provide a map and cross-sections showing the distribution of free or residual product;
- identification of the treatment radius and how it was determined;
- identification of when the reagent was exhausted and how that was determined;
- a recalculation of ground water seepage velocity to determine if sufficient time has passed to reach down-gradient wells;
- the post remedial sampling results for soil, ground water and any other media sampled as part of an IRM, source control, PBR compliance and RAW implementation; and
- a copy of any PBR compliance report(s) that previously had to be submitted.

The investigator is reminded that the Department's PBR discharge approval (i.e., authorization) letter is not an approval of the RAW; it is only an approval of the DGW proposal. For UHOT Cases, as was indicated in Section 5.4 above, any post remedial soil and or ground water sampling should have been discussed with the assigned BFO case manager prior to completion.

If performance monitoring extends into the Remedial Action Permit phase, reporting can be conducted within the biennial certification and report submission as indicated in Section 7.3.2.

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## APPENDIX A – PARAMETERS AND EQUATIONS

Equations that can be used in the design of in situ soil and/or ground water remedial actions, and to verify that the in situ injections were performed as proposed/designed are presented below. Separate equations are provided below for unsaturated soils and saturated soils and groundwater. Site-specific soil porosity ( $n$ ), soil effective porosity ( $n_e$ ), soil hydraulic conductivity ( $k$ ), soil fraction organic carbon ( $foc$ ), and treatment reagent(s) viscosity ( $\mu$ ), should be used in the calculations. However, literature values of approximate ranges of porosity, effective porosity and hydraulic conductivity are provided below to aid the investigator if site-specific values are not available (Bouwer, 1978; McWhorter and Sunada, 1977; NJGS, 2003). Alternatively, see the Literature Review (Section 3.1.3.3) in the Department’s Ground Water Technical Guidance for additional resources ([http://www.nj.gov/dep/srp/guidance/srra/gw\\_inv\\_si\\_ri\\_ra.pdf](http://www.nj.gov/dep/srp/guidance/srra/gw_inv_si_ri_ra.pdf)).

### Porosity

| <u>Formation Material</u>                         | <u>Porosity</u> |
|---|-----------------|
| Clays   | 50 -- 60 %      |
| Silts   | 50 -- 60 %      |
| Fine sand   | 40 -- 50 %      |
| Medium sand                                       | 35 -- 40 %      |
| Coarse sand                                       | 25 -- 35 %      |
| Gravel  | 20 -- 30 %      |
| Sand and gravel mixes                             | 10 -- 30 %      |
| Glacial till                                      | 25 -- 45 %      |
| Fractured and weathered igneous rock              | 2 -- 10 %       |
| Fractured and weathered shale                     | 2 -- 10 %       |
| Sandstone   | 5 -- 30 %       |
| Carbonate rock w/ original and secondary porosity | 10 -- 20 %      |

| <u>Formation Material</u> | <u>Porosity</u> | <u>Effective Porosity</u> |
|---------------------------|-----------------|---------------------------|
| Clay                      | 42 %            | 6 %                       |
| Silt                      | 46 %            | 20 %                      |
| Fine sand                 | 43 %            | 33 %                      |
| Medium sand               | -----           | 32 %                      |
| Coarse sand               | 39 %            | 30 %                      |
| Fine Gravel               | 34 %            | 28 %                      |
| Medium Gravel             | -----           | 24 %                      |
| Coarse Gravel             | 28 %            | 21 %                      |
| Sandstone                 | 34 %            | -----                     |
| Fine Sandstone            | -----           | 21 %                      |
| Medium Sandstone          | -----           | 27 %                      |
| Siltstone                 | 35 %            | 12 %                      |
| Limestone                 | 30 %            | 14 %                      |

| <u>Formation Material</u>   | <u>Hydraulic Conductivity</u>  |
|-----------------------------|--------------------------------|
| Clay soils (surface)        | 0.03 -- 0.6 feet/day           |
| Deep clay beds              | 0.00000003 -- 0.03 feet/day    |
| Silty clay                  | 0.03 -- 3 feet/day             |
| Loam soils                  | 0.3 -- 3 feet/day              |
| Fine sand                   | 3 -- 15 feet/day               |
| Medium sand                 | 15 -- 65 feet/day              |
| Coarse sand                 | 65 -- 330 feet/day             |
| Kirkwood-Cohansey Formation | 22 -- 365 feet/day (NJGS 2003) |
| Gravel                      | 330 -- 3280 feet/day           |

|  |                       |
|--|-----------------------|
| Sand and gravel mixes                  | 15 -- 330 feet/day    |
| Clay, sand and gravel mixes (till)     | 0.003 -- 0.3 feet/day |
| Sandstone                              | 0.003 -- 3 feet/day   |
| Carbonate rock with secondary porosity | 0.03 -- 3 feet/day    |
| Shale                                  | 0.0000003 feet/day    |
| Fractured or weathered rock (aquifers) | 0.003 -- 33 feet/day  |

### **Equations for In situ Soil Remedial Actions**

To optimize the effectiveness of the in situ design, treatment reagents solutions or slurries injected into the unsaturated-zone and vadose-zone, must be in contact with the contaminants being remediated. This requires that the treatment solutions or slurries injected must completely fill the pore volume of the contaminated unsaturated-zone and vadose-zone. Therefore, the porosity and effective porosity of the soil being treated must be known in order to determine the quantities of treatment solutions or slurries that should be injected, and to verify that sufficient quantities of treatment solutions or slurries were actually injected.

- 1) The following equation can be used to determine the volume of treatment reagent(s) solution/slurry that should be injected at an injection well location to achieve the proposed/designed radius-of-influence (based on the equation for the volume of a cylinder):

$$V_{TS} \approx 3.14159 * (ROI_P)^2 * (D_B - D_T) * n_e * 7.48$$

Where:

$V_{TS}$  = Volume of treatment solution/slurry required to achieve proposed/designed radius-of-influence (in units of gallons);

3.14159 = Pi

$ROI_P$  = Proposed radius-of-influence (in units of feet);

$D_B$  = Depth to bottom of in situ treatment zone (in units of feet);

$D_T$  = Depth to top of in situ treatment zone (in units of feet);

$n_e$  = Effective porosity of soil (decimal equivalent, not a percentage);

7.48 = Conversion factor to convert volume from cubic feet to gallons;

\* = Multiplication;

( )<sup>2</sup> = Square.

- 2) The following equation can be used to determine the actual radius-of-influence that was achieved at an injection well location based upon the actual volume of treatment reagent(s) solution/slurry injected as recorded in the field log for the injection event (based on the equation for the volume of a cylinder):

$$ROI_A \approx ( \{ V_{TSI} \} / \{ 3.14159 * (D_B - D_T) * n_e * 7.48 \} )^{1/2}$$

Where:

$ROI_A$  = Actual radius-of-influence achieved (in units of feet);

$V_{TSI}$  = Actual volume of treatment solution/slurry injected at an injection location (in units of gallons);

3.14159 = Pi

$D_B$  = Depth to bottom of in situ treatment zone (in units of feet);

$D_T$  = Depth to top of in situ treatment zone (in units of feet);

$n_e$  = Effective porosity of soil (decimal equivalent, not a percentage);

7.48 = Conversion factor to convert volume from cubic feet to gallons;

/ = Division;

\* = Multiplication;

( )<sup>1/2</sup> = Square root.

- 3) The following equation can be used to determine the total mass of a soil contaminant within a cylindrical volume of soil with the proposed/designed radius-of-influence surrounding an injection well (based on the equation for the volume of a cylinder):

$$M_{CON} \approx 3.14159 * (ROI_P)^2 * (D_B - D_T) * (1.0 - n) * 0.02832 * 2650 * C_{CON} * 0.0000022$$

Where:

$M_{CON}$  = The total mass of soil contaminant within the proposed/designed radius-of-influence (in units of pounds);

3.14159 = Pi

$ROI_P$  = Proposed radius-of-influence (in units of feet);

$D_B$  = Depth to bottom of in situ treatment zone (in units of feet);

$D_T$  = Depth to top of in situ treatment zone (in units of feet);

$n$  = Porosity of soil (decimal equivalent, not a percentage);

0.02832 = Conversion factor to convert cubic feet to cubic meters;

2650 = Density of solid rock (in units of kilograms/cubic meter);

$C_{CON}$  = Concentration of soil contaminant (in units of milligrams/kilogram);

0.00000220462 = Conversion factor to convert milligrams to pounds;

\* = Multiplication;

( )<sup>2</sup> = Square.

- 4) The following equation can be used to determine the total mass of an in situ treatment reagent required to treat the cylindrical volume of contaminated soil within the proposed/ designed radius-of-influence surrounding an injection well:

$$M_{TR} \approx AR_{TR} * M_{CON}$$

Where:

$M_{TR}$  = Total mass of treatment reagent required to treat the soil contaminant within the proposed/ designed radius-of-influence (in units of pounds);

$AR_{TR}$  = The application rate of the treatment reagent, which is the number of pounds of treatment reagent required to treat one (1) pound of contaminant (in units of pounds/pound), this information should be provided by the treatment reagent(s) manufacturer/supplier;

$M_{CON}$  = The total mass of soil contaminant within the proposed/ designed radius-of-influence (in units of pounds) (see calculation above);

\* = Multiplication.

- 5) The following equation can be used to determine the concentration of the treatment reagent in the solution/slurry required to treat the cylindrical volume of contaminated soil within the proposed/ designed radius-of-influence surrounding an injection well:

$$C_{TR} \approx M_{TR} / V_{TS}$$

Where:

$C_{TR}$  = Concentration of treatment reagent in the solution/slurry required to treat the soil contamination within the proposed/designed radius-of-influence (in units of pounds/gallon);

$M_{TR}$  = Total mass of treatment reagent required to treat the soil contaminant within the proposed/designed radius-of-influence (in units of pounds) (see calculation above);

$V_{TS}$  = Volume of treatment solution/slurry required to achieve proposed/designed radius-of-influence (in units of gallons) (see calculation above);

/ = Division.

### **Equations for In Situ Ground Water Remedial Actions**

To be effective, the total mass of the treatment reagent(s) in the solution/slurry to be injected must be sufficient to treat the total contaminant mass within the cylindrical volume of the formation within the proposed/designed radius-of-influence. In addition, the effectiveness depends on a sufficiently long injection duration to allow the treatment reagent(s) solution/slurry to disperse/mix into the entire cylindrical volume of the proposed/designed radius-of-influence.

- 1) The following equation can be used to determine the total dissolved mass of a ground water contaminant within a cylindrical volume of a formation within the proposed/designed radius-of-influence surrounding an injection well (this equation is based on the volume of a cylinder):

$$M_{D-CON} \approx 3.14159 * (ROI_P)^2 * (D_B - D_T) * n * 28.3168 * C_{CON} * 0.00000000220462$$

Where:

$M_{D-CON}$  = The total dissolved mass of a ground water contaminant within the proposed/designed radius-of-influence (in units of pounds);

3.14159 = Pi

$ROI_P$  = Proposed radius-of-influence (in units of feet);

$D_B$  = Depth to bottom of in situ treatment zone (in units of feet);

$D_T$  = Depth to top of in situ treatment zone (in units of feet);

n = Porosity of aquifer material (decimal equivalent, not a percentage);

28.3168 = Conversion factor to convert cubic feet to liters;

$C_{CON}$  = Concentration of ground water contaminant (in units of micrograms/liter);

0.00000000220462 = Conversion factor to convert micrograms to pounds;

\* = Multiplication;

( )<sup>2</sup> = Square.

2) The following equation can be used to determine the total adsorbed mass of a ground water contaminant within a cylindrical volume of the formation within the proposed/designed radius-of-influence surrounding an injection well (this equation is based on the volume of a cylinder):

$$M_{A-CON} \approx 3.14159 * (ROI_P)^2 * (D_B - D_T) * (1.0 - n) * 0.02832 * 2650 * foc * C_{CON} * 0.001 * Koc * 0.0000022$$

Where:

$M_{A-CON}$  = The total adsorbed mass of a ground water contaminant within the proposed/designed radius-of-influence (in units of pounds);

3.14159 = Pi

$ROI_P$  = Proposed radius-of-influence (in units of feet);

$D_B$  = Depth to bottom of in situ treatment zone (in units of feet);

$D_T$  = Depth to top of in situ treatment zone (in units of feet);

n = Porosity of aquifer material (decimal equivalent, not a percentage);

0.02832 = Conversion factor to convert cubic feet to cubic meters;

2650 = Density of solid rock (in units of kilograms/cubic meter);

foc = Fraction of organic carbon (in units of kilograms/kilogram);

$C_{CON}$  = Concentration of ground water contaminant (in units of micrograms/liter);

0.001 = Conversion factor to convert from micrograms to milligrams;

Koc = Soil-water partition coefficient for ground water contaminant (in units of liters/kilogram);

0.0000022 = Conversion factor to convert milligrams to pounds;

\* = Multiplication;

( )<sup>2</sup> = Square.

- 3) The following equation can be used to determine the total dissolved plus adsorbed mass of a ground water contaminant within a cylindrical volume of the formation within the proposed/designed radius-of-influence surrounding an injection well:

$$M_{T-CON} \approx M_{D-CON} + M_{A-CON}$$

Where:

$M_{T-CON}$  = The total dissolved plus adsorbed mass of a ground water contaminant within the proposed/designed radius-of-influence (in units of pounds);

$M_{D-CON}$  = The total dissolved mass of a ground water contaminant within the proposed/designed radius-of-influence (in units of pounds) (see equation above);

$M_{A-CON}$  = The total adsorbed mass of a ground water contaminant within the proposed/designed radius-of-influence (in units of pounds) (see equation above).

- 4) The following equation can be used to determine the total mass of an in situ treatment reagent required to treat the cylindrical volume of contaminated ground water within the proposed/designed radius-of-influence surrounding an injection well:

$$M_{TR} \approx AR_{TR} * M_{T-CON}$$

Where:

$M_{TR}$  = The total mass of treatment reagent required to treat a ground water contaminant within the proposed/designed radius-of-influence (in units of pounds);

$AR_{TR}$  = The application rate of the treatment reagent, which is the number of pounds of treatment reagent required to treat one (1) pound of contaminant (in units of pounds/pound) -- this information should be provided by the treatment reagent(s) manufacturer/supplier;

$M_{CON}$  = The total mass of a ground water contaminant within the proposed/designed radius-of-influence (in units of pounds) (see equation above);

\* = Multiplication.

- 5) The following equation can be used to determine the total time the treatment reagent(s) solution/slurry injection should occur in order to achieve the proposed radius-of-influence (this equation is based on Darcy's Law):

$$T_{INJ} \approx ROI_P / \left( \left( (DTGW + H + (P_{INJ} * 2.31)) / ROI_P \right) * \{k_{HC} * 0.04167 * (1.0 / \mu_{TR})\} / n_e \right)$$

Where:

$T_{INJ}$  = Total injection time required to achieve the proposed radius-of-influence (in units of hours);

$ROI_P$  = Proposed radius-of-influence (in units of feet);

$DTGW$  = Depth to ground water (in units of feet);

$H$  = The height (above ground surface) of the “stick-up” of the well casing of the permanent/temporary injection well being injected into, or the height (above ground surface) of the top of the string of probe-rods being injected into (in units of feet);

$P_{INJ}$  = The pressure the treatment reagent(s) solution/slurry is being injected at (in units of pounds/square inch) --  $P_{INJ}$  should equal zero if the treatment reagent(s) solution/slurry is only being gravity-fed into the well casing/probe-rods and no additional pressure is being applied to the solution/slurry being injected;

2.31 = Conversion factor to convert pounds/square inch to feet of water;

$k_{HC}$  = Hydraulic conductivity of the formation material (in units of feet/day);

0.04167 = Conversion factor to convert feet/day to feet/hour;

1.0 = Viscosity of water @ 20°C (in units of centipoise);

$\mu_{TR}$  = Viscosity of the treatment reagent(s) solution/slurry @ 20°C (in units of centipoise) -- this information should be provided by the treatment reagent(s) manufacturer/supplier;

$n_e$  = Effective porosity of formation material (decimal equivalent, not a percentage);

\* = Multiplication;

/ = Division.

- 6) The following equation can be used to determine the actual radius-of-influence that was achieved at an injection well location based upon the total time the treatment solution/slurry was injected, as recorded in the field log for the injection event (this equation is based on Darcy’s Law):

$$ROI_A \approx ((DTGW + H + (P_{INJ} * 2.31)) / ROI_P) * \{k_{HC} * 0.04167 * (1.0 / \mu_{TR})\} / n_e * T_{INJ}$$

Where:

$ROI_A$  = Actual radius-of-influence achieved (in units of feet);

$DTGW$  = Depth to ground water (in units of feet);

$H$  = The height (above ground surface) of the “stick-up” of the well casing of the permanent/temporary injection well being injected into, or the height (above ground surface) of the top of the string of probe-rods being injected into (in units of feet);

$P_{INJ}$  = The pressure the treatment reagent(s) solution/slurry is being injected at (in units of pounds/square inch) --  $P_{INJ}$  should equal zero if the treatment reagent(s) solution/slurry is only being gravity-fed into the well casing/probe-rods and no additional pressure is being applied to the solution/slurry being injected;

2.31 = Conversion factor to convert pounds/square inch to feet of water;

$ROI_P$  = Proposed radius-of-influence (in units of feet);

$k_{HC}$  = Hydraulic conductivity of the formation material (in units of feet/day);

0.04167 = Conversion factor to convert feet/day to feet/hour;

1.0 = Viscosity of water @ 20°C (in units of centipoise);

$\mu_{TR}$  = Viscosity of the treatment reagent(s) solution/slurry @ 20°C (in units of centipoise) -- this information should be provided by the treatment reagent(s) manufacturer/supplier;

$n_e$  = Effective porosity of the formation material (decimal equivalent, not a percentage);

$T_{INJ}$  = Total time the treatment solution/slurry was injected (in units of hours);

\* = Multiplication;

/ = Division.

## APPENDIX B – FIELD PARAMETERS AND ENTRIES FOR FIELD LOGS

**Field Parameters** - Parameters analyzed in the field, including pH, dissolved oxygen, oxidation-reduction potential (ORP), temperature, and conductivity, are to be measured by a certified contractor or laboratory as required by N.J.A.C. 7:26E-2.1(a)1 and N.J.A.C. 7:18 or as required by N.J.A.C. 7:26E-2.1(a)2. Section 6.9.8 Ground Water-Level Measurements in the Department’s Field Sampling Procedures Manual provides guidance regarding measuring the depth to ground water.

**Recommended Field Log Entries** - For injections via permanent or temporary injection wells either individually or manifolded together -- the injection contractor should log the following information for **each** permanent/temporary injection well:

- 1) The total length of the screened interval being injected into, the depths of the top and bottom of the screened interval being injected into, and the height of the “stick-up” of the injection well casing above the ground surface;
- 2) The total volume of treatment reagent(s) solution/slurry injected;
- 3) The concentration(s) of the treatment reagent(s) in the solution/slurry being injected (e.g., lbs. per gallon of solution);
- 4) The start time and stop time of the injection;
- 5) Note whether the treatment solution/slurry was gravity-fed into the injection well;
- 6) Note whether the treatment solution/slurry was injected under pressure, and if so, what the injection pressure was;
- 7) Note whether surfacing/day-lighting of treatment reagent(s) occurred, and if so, what volume of solution/slurry had already been injected at the time surfacing/day-lighting of the treatment reagent(s) was observed;
- 8) If treatment reagents, concentrations, and/or rates are changed during the injection, record the time(s) of and change(s) to each parameter (e.g., two hours into a four hour injection the concentration of ferrous sulfate was increased from 1 lb. per gallon to 2 lbs per gallon with the injection rate remaining the same at 5 gallons per minute).

For injections via the open end of the probe-rods as the probe-rods are being extracted from the borehole, the Department recommends the injection contractor log the following information for each injection location:

- 1) The total length of borehole over which the injection occurred, and the depths of the top and bottom of the vertical interval over which the injection occurred;

- 2) At each borehole, a list of the depth intervals at which the injection occurred, including the injection start times and stop times at each interval and the associated volumes of reagent(s) solution/slurry injected at each interval;
- 3) The total volume of treatment reagent(s) solution/slurry injected per borehole (assuming injections occurred in multiple depth intervals per borehole) and total volume for the entire treatment area;
- 4) Concentration(s) of the treatment reagent(s) in the solution/slurry being injected (e.g., lbs. per gallon of solution);
- 5) Note whether the treatment solution/slurry was being gravity-fed into the top of the string of probe-rods;
- 6) Note whether the treatment solution/slurry was being injected into the probe-rods under pressure, and if so, what the injection pressure was;
- 7) Note whether surfacing/day-lighting of treatment reagent(s) occurred, and if so, what the depth of the bottom of the probe-rods was at the time surfacing/day-lighting of the treatment reagent(s) was observed, and what volume of solution/slurry had already been injected at the time surfacing/day-lighting of the treatment reagent(s) was observed.

**General Note:** Any surfacing/day-lighting, or other malfunctions relating to the injections, are to be reported to the Department as a condition of the NJPDES DGW permit-by-rule.

**Field Surfactant Testing (Shaker Test)** - For anionic surfactants, a field test to determine whether foaming agents (ABS/LAS) are present in ground water can be performed as follows: (1) Half-fill a clear jar, with a sealable lid, with ground water to be tested, (2) Vigorously shake/agitate the closed jar with the ground water sample for 10 to 15 seconds, (3) If the agitated water becomes foamy/frothy, the water sample may contain foaming agents at concentrations which could exceed the GWQS for foaming agents (ABS/LAS) of 500 ug/l. The investigator should include the results and date in a field log for each well or location tested. Shaker tests can be used to confirm the presence of foaming agents, but cannot replace or satisfy the requirement for laboratory analysis to confirm compliance with the GWQS.

## APPENDIX C – MONITORING FOR COMMON REAGENT PRODUCTS

For monitoring recommendations or requirements, see Section 6 and applicable table number listed below and Section 7.1 for PBR/DGW proposal requirements.

| Supplier                                | Injectant / reagent product   | Notes/Additional Information  | Table Number |
|---|---|---|--------------|
| Terra Systems, Inc. or RNAS Remediation | Emulsified vegetable oil (EVO)  | Anaerobic and Reduction Technology  | 1 & 7        |
| various                                 | Molasses – Bulk   | Anaerobic Technology  | 1            |
| various                                 | Oxygen –releasing substances  | Aerobic Technology  | 2            |
| various                                 | Microorganisms – bacteria<br>Dehalococcoides (DHC)- strains and others, e.g.,<br>Dehalobacter (DHB) | Anaerobic Technology  | 1            |
| CL Solutions                            | Petrox 1, 2 and 3   | Aerobic Technology  | 2            |
| ETEC                                    | CarBstrate™, nutrient-amended carbohydrate  | Anaerobic Technology  | 1            |
| Remediation Products, Inc.              | Trap & Treat BOS 200  | Activated carbon slurry with sulfate and micronutrients. Petroleum hydrocarbon biological degradation in aerobic or anaerobic conditions. | 1 & 2        |
|   | Trap & Treat BOS 100  | Chemical reduction via a slurry of activated carbon impregnated with metallic iron.   | 7            |

| Company              | Product                   | Notes/Additional Information          | Table Number |
|----------------------|---------------------------|---------------------------------------|--------------|
| Tersus Environmental | TASK – DRO and – GRO      | Anionic surfactant (MBAS Analysis)    | 5            |
| SuperAll Product LLC | Superall #38, TopsAll #30 | Anionic surfactant                    | 5            |
| The BioSolve Company | BioSolve® Pinkwater       | Non- ionic surfactant (CTAS Analysis) | 5            |
| Simple Green         | Simple Green Crystal      | Non-ionic surfactant                  | 5            |

|  |                               |                                     |   |
|--|-------------------------------|-------------------------------------|---|
| Procter and Gamble, or Colgate-Palmolive | Dawn detergent                | Non-ionic surfactant (also anionic) | 5 |
| Environmental Chemical Solutions         | Accelerate Gold Crew REM-E001 | Non-ionic surfactant                | 5 |
| EnviroSupply & Service, Inc.             | Ivey-sol (MSDS # 120829)      | Non-ionic surfactant                | 5 |

| <b>Supplier</b>   | <b>Injectant / reagent product</b>                                | <b>Notes/Additional Information</b>  | <b>Table Number</b> |
|---|---|--|---------------------|
| PeroxyChem (formerly Adventus Remediation Technologies, Inc.) | EHC-Liquid Reagent  | Liquid formula for wells   | 1 & 7               |
|   | EHC- ISCR Reagent   | Anaerobic degradation of VOCs, pesticides & energetics & metals immobilization.            | 1 & 7               |
|   | EHC-Metals Reagent  | Immobilization of metals   | 7                   |
|   | PermeOx Ultra   | Aerobic Bioremediation (Bio), O2 release   | 2                   |
|   | ELS Microemulsion   | Carbon source for anaerobic bioremediation   | 1                   |
|   | MetaFix Reagents  | Reduction technology for metals and chlorinated solvents                                   | 7                   |
|   | TERRAMEND Reagent   | Aerobic Bio applied to soils   | 2                   |
| PeroxyChem (formerly FMC Corp.)                               | DARAMEND Reagent  | Amended with zero-valent iron (ZVI), sodium sulfite, yeast extract and calcium propionate. | 1 & 7               |
|   | Klozur SP   | Oxidant  | 6                   |
| Regenesis   | Klozur CR - sodium persulfate & PermeOx Ultra                     | Oxidant & aerobic bioremediation   | 2 & 6               |
|   | ORC & ORC Socks & Canisters                                       | Aerobic Bio  | 2                   |
|   | ORC Advanced  | Aerobic Bio  | 2                   |
|   | ORC Advanced Pellets  | Aerobic Bio  | 2                   |
|   | 3-D Microemulsion (3-DME) & 3-DME Factory Emulsified              | Anaerobic Bio  | 1                   |
| Hydrogen Release Compound (HRC), HRC-X, HRC Primer            | Anaerobic Bio – all have a similar chemical content but HRC/HRC-X | 1  |                     |

|   |   |   |       |
|---|---|---|-------|
|   |   | has a pH of 3; HRC Primer pH is 2 and it is less viscous.   |       |
|   | Chemical Reducing Solution (CRS)                            | Chemical reduction via biotic and abiotic pathways using ferrous gluconate, neutral pH  | 7     |
|   | Metals Remediation Compound (MRC)                           | Organosulfur compound that produces reducing conditions; pH of 3, strong amine or sulfur odor.  | 7     |
|   | Bio-Dechlor Inoculum Plus                                   | Anaerobic Bioaugmentation   | 1     |
|   | RegenOx – Parts A & B                                       | Oxidant - sodium percarbonate, silicic acid, sodium silicates, silica gel & ferrous sulfate   | 6     |
|   | PersulfOx & PersulfOx SP                                    | Oxidant – sodium persulfate & sodium silicate   | 6     |
|   | PetroCleanze  | Enhanced Desorption – contains silicic acid, sodium salt, sodium silicate, ferrous sulfate, sodium hydroxide & sodium tripolyphosphate; used with RengenOx Part A | 5 & 6 |
|   | PlumeStop Liquid Activated Carbon                           | Very fine particles of activated carbon used in aerobic or anaerobic conditions to enhance bioremediation. pH is 8-10.  | 1 & 2 |
| Redox Tech LLC                              | Oxygen BioChem (OBC™)                                       | Oxidant - sodium persulfate and calcium peroxide  | 6     |
|   | Oxygen BioChem (OBC+)                                       | BioChemical – includes magnesium sulfate (Epsom salts/MgSO4) to enhance biological oxidation under anaerobic/reducing conditions                                  | 1&7   |
| Lagacy Environmental Services, LLC          | IPC-14FR, sodium percarbonate with catalytic process (APOx) | Oxidant   | 6     |
| Gitech, LLC or Continental Remediation, LLC | NanoPeroxide™   | Oxidant   | 6     |

|         |  |                               |   |
|---------|--|-------------------------------|---|
| various | Calcium polysulfide (CaSx)               | Chemical metal reduction Cr+6 | 7 |
| various | Citrix acid stabilized hydrogen peroxide | Oxidant                       | 6 |

## APPENDIX D - ACRONYMS

|             |   |
|-------------|---|
| ACoE –      | Army Corp of Engineers  |
| AOC –       | area of concern   |
| ARRCS –     | Administrative Requirements for the Remediation of Contaminated Sites |
| AS –        | air sparging  |
| ASTM –      | American Society for Testing and Materials                            |
| BTEX –      | benzene, toluene, ethylbenzene, and xylenes                           |
| CAH –       | chlorinated aliphatic hydrocarbons                                    |
| CEA –       | classification exception area   |
| Cis-1,2-DCE | –cis-1,2-Dichloroethene   |
| COC –       | contaminant of concern  |
| CSM –       | conceptual site model   |
| CT –        | carbon tetrachloride  |
| DCP –       | 1,2-dichloropropane   |
| DGW –       | discharge to ground water   |
| DHB –       | dehalobacter  |
| DHC –       | dehalococoides  |
| DHG –       | dehalogenimonas   |
| DNAPL –     | dense non-aqueous phase liquid  |
| DO –        | dissolved oxygen  |
| EPH –       | extractable petroleum hydrocarbons                                    |
| ERH –       | electrical resistance heating   |
| EPA –       | Environmental Protection Agency                                       |

|            |   |
|------------|---|
| FRTR -     | Federal Remediation Technologies Roundtable       |
| GWQS –     | ground water quality standard                     |
| IEC –      | immediate environmental concern                   |
| IRM –      | interim remedial measure                          |
| ISCO –     | in situ chemical oxidation                        |
| ISCR –     | in situ chemical reduction                        |
| ITRC –     | Interstate Technology & Regulatory Council        |
| IWAS –     | in-well air stripping                             |
| LSRP –     | licensed site remediation professional            |
| MNA –      | monitored natural attenuation                     |
| MTBE –     | methyl tertiary-butyl ether                       |
| MSDS –     | material safety data sheets                       |
| NAPL –     | non-aqueous phase liquid                          |
| N.J.A.C. – | New Jersey Administrative Code                    |
| NJDEP –    | New Jersey Department of Environmental Protection |
| NJPDES –   | New Jersey Pollutant Discharge Elimination System |
| ORP –      | oxidation-reduction potential                     |
| PAH –      | polycyclic aromatic hydrocarbon                   |
| PBR –      | permit-by-rule                                    |
| PCB –      | polychlorinated biphenyls                         |
| PCE –      | perchloroethene or tetrachloroethylene            |
| pH -       | potential of hydrogen                             |
| PID –      | photo ionization device                           |
| POET –     | point of entry treatment                          |

|         |   |
|---------|---|
| PRB –   | permeable reactive barrier                    |
| RA –    | remedial action                               |
| RAP –   | remedial action permit                        |
| RAW –   | remedial action workplan                      |
| RI –    | remedial investigation                        |
| RIR –   | remedial investigation report                 |
| ROI –   | radius of influence                           |
| SEE –   | Steam Enhanced Extraction                     |
| SRP –   | Site Remediation Program                      |
| SVE –   | soil vapor extraction                         |
| SVOC –  | semi volatile organic compounds               |
| SWQS –  | surface water quality standards               |
| TCE –   | trichloroethene                               |
| TCH –   | thermal conduction heating                    |
| TCLP –  | toxicity characteristic leaching procedure    |
| TCP –   | 1,2,3-trichloropropane                        |
| TOC –   | total organic carbon                          |
| USEPA – | United States Environmental Protection Agency |
| UST –   | underground storage tank                      |
| VC –    | vinyl chloride                                |
| VIT –   | vapor intrusion technical guidance            |
| VOCs –  | volatile organic compounds                    |
| ZVI –   | zero valent iron                              |